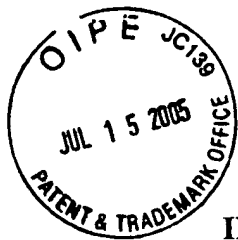


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Serial No. 10/605,332
Page 1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PATENT application of:

Applicants: Peter J. Nicklas
Application No.: 10/714,090
For: HYBRID TUBULAR WIRE ELECTRODE
FOR SUBMERGED ARC WELDING
Filing Date: November 14, 2003
Publication Number: US 2005/0103751 A1
Publication Date: May 19, 2005

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THIRD PARTY SUBMISSION IN PUBLISHED APPLICATION UNDER 37 CFR 1.99

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

The patents listed below are relevant to the above referenced published application, copies of which are enclosed herewith:

U.S. Patents
Suzuki 3,924,091

Publication Date
December 2, 1975

Japanese Patents
Masahiko JP 58135793
(with translation of Table 1
and Abstract)
Title: Flux Cored Wire for
Submerged Arc Welding

Publication Date
1983

Masao JP 63212092
(with translation of the heading
of Table 1 and Abstract)
Title: Seamless Flux Cored
Wire for Submerged Arc
Fillet Welding

1988

OK to enter
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QUALITY ASSURANCE SPECIALIST

Also enclosed herewith is the fee of \$180.00 as set forth in 37 CFR 1.17(p).

10/03/05 10/03/05 10/03/05 10/03/05 10/03/05 10/03/05 10/03/05 10/03/05 10/03/05 10/03/05

This submission is being filed within two months of the date of publication of the above referenced published application and prior to the mailing of a notice of allowance in accordance with 37 CFR 1.99(e).

Enclosed with this submission is a self-addressed postcard in accordance with 37 CFR 99(f).

PROOF OF SERVICE:

In accordance with 37 CFR 1.99(c) and 37 CFR 1.248(a)(4), this submission, including copies of the above listed references, has been transmitted this date May 23, 2005 by first class mail to the attorneys of record in the above published application addressed to:

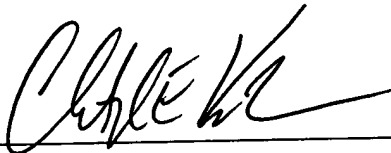
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7/15/05

Date



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(19) United States

(12) Patent Application Publication

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Nicklas

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May 19, 2005

(54) HYBRID TUBULAR WIRE ELECTRODE
FOR SUBMERGED ARC WELDING

(52) U.S. Cl. 219/73; 219/145.22

(75) Inventor: Peter J. Nicklas, Troy, OH (US)

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ABSTRACT

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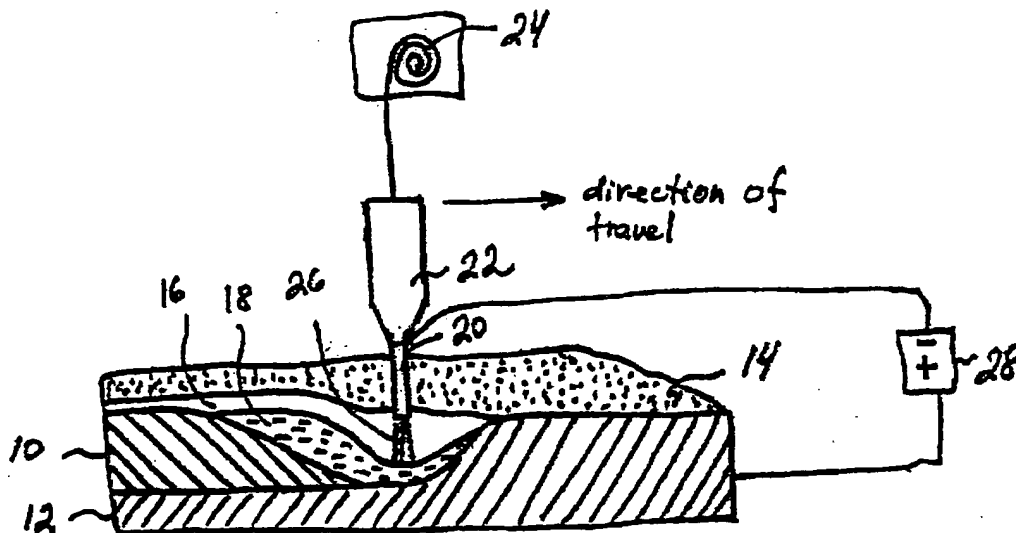
(21) Appl. No.: 10/714,090

(22) Filed: Nov. 14, 2003

Publication Classification

(51) Int. Cl.⁷ B23K 9/18

The hybrid wire of the present invention comprises approximately 1% Wt to 30% Wt of non-metallic ingredients, with the preferred concentrations selected from the range from about 5% Wt to about 15% Wt. Non-metallic compounds and metallic oxides, which were added to the tubular wires and found to perform well in the SAW process, are CaO, MgO, MgAl, K₂O, CaF₂, MnO, NaAlF₆, and K₂AlF₆. Adding one or more of the listed compounds to the core composition of the tubular wires leads to an improvement of the welding performance in a SAW process due to the properties of core of the wire, while reducing the importance of the granular flux.



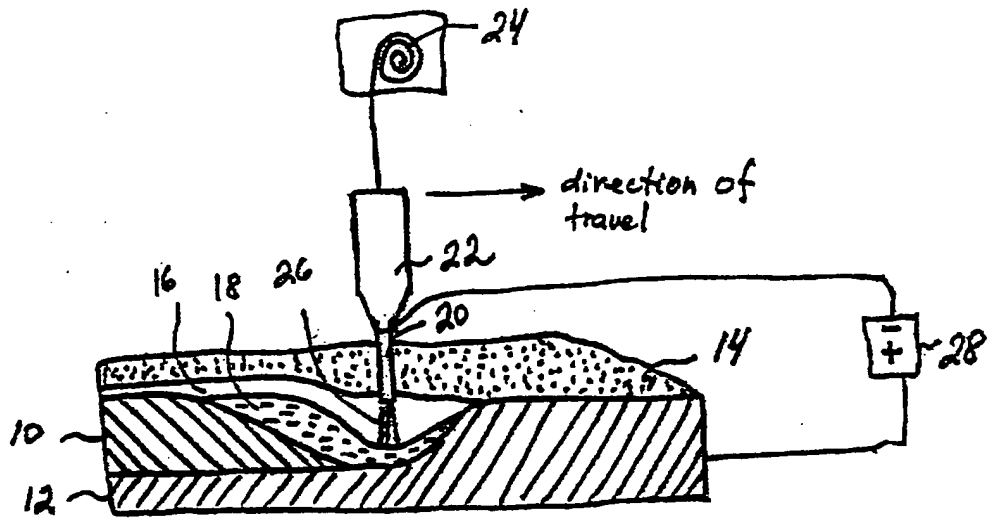


Fig. 1

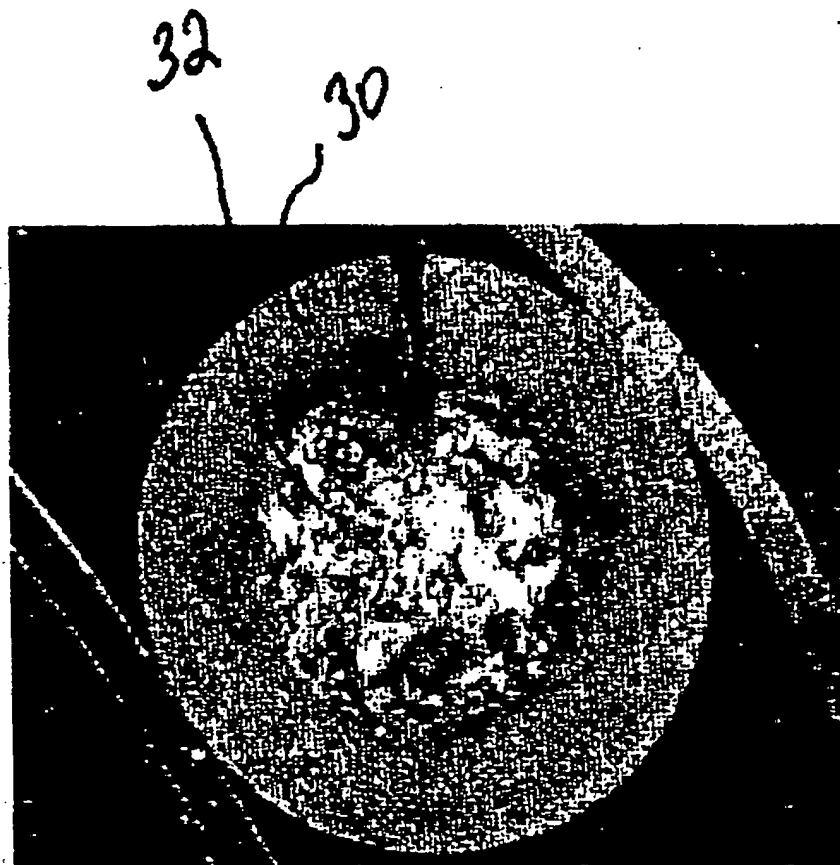


Fig. 2

Table 1.

Raw material	047N-01-003	047N-03-001	047N-03-002	047N-03-003	047N-03-006	047N-03-007	047N-03-008	047N-03-009	047N-03-010	047N-03-011
Fe Powder	83.65	77.25	73.25	73.25	90.75	90.25	87.75	83.25	81.25	61.25
Ferro Mg, Hi C	3.75	3.75	3.75	3.75	3.75	3.75	3.75	3.75	3.75	3.75
Ferro Si	1.60	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Alumina, Al ₂ O ₃		7.00	7.00	7.00	0.50	0.50	1.00	3.00	3.00	7.00
Alumina, Al ₂ O ₃ with Na ₂ O ₃		7.00	7.00	7.00		0.50	0.50	3.00	3.00	7.00
MgCO ₃										1.00
MgAl, 40x200m				4.00			2.00		2.00	4.00
CaF ₂								2.00		4.00
MgAl, -200m			4.00						2.00	4.00
CaCO ₃	4.00									1.00
Fluorspar, CaF ₂	5.00									2.00
MgO	2.00									30.00
Approx slag, %	11.00	14.00	18.00	18.00	0.50	1.00	3.50	8.00	10.00	100.00
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Fig. 3

Table 2

Flux Composition	Wt%
Bauxite/ Al_2O_3	30%
Fluorides	15%
Silicates and binders	10%
Magnesite	10%
Manganese Compounds	10%
Quartz, SiO_2	5%
Silicon	<5%
Mineral Silicates	<5%
Iron	<5%

Fig. 4

Deposit Chemistries

Table 3

Element	Carbon Steels	Low Alloy Steels
C	0.15	0.15
Mn	1.80	2.10
Si	0.90	0.80
P	0.030	0.030
S	0.030	0.030
Cr	-	8.0
Ni	-	4.0
Mo	-	1.0
Cu	0.30	0.75
Ti +V+Zr	-	0.030

Fig. 5

HYBRID TUBULAR WIRE ELECTRODE FOR SUBMERGED ARC WELDING

FIELD OF THE INVENTION

[0001] The present invention relates to the field of submerged arc welding. More specifically, the invention relates to compositions of a hybrid tubular wire electrode enhancing the performance of wire/flux combination used in the submerged arc welding process.

BACKGROUND OF THE INVENTION

[0002] Submerged arc welding (SAW) is a process in which joining of metal pieces is accomplished by heating the metal pieces with an arc existing between an electrode and the metal. In the submerged arc welding process the arc and the molten metal are shielded from the atmospheric oxygen and nitrogen by a blanket of fusible granular flux, which covers the arc. The welding electrode of the submerged arc welding process is a consumable wire electrode continuously fed to the welding process. The flux covering the arc significantly reduces spatter, smoke, and arc flashes, allowing higher utilization the wire electrode at higher welding speeds and deposition rates.

[0003] The consumable wire electrodes used in the SAW process are predominantly solid carbon or low alloy steel electrodes, where a specific combination of the wire/flux composition is required for the optimal performance and weld quality. Most of the oxides and compounds incorporated into the flux cannot be added during the steelmaking process because of the differences in the melting temperatures and the problem with their solubility in steel. The resulting metal would have gross inclusions and be very weak. The solution to the problem is to use tubular wire electrodes consisting of a mild steel sheath and a core composition comprising desired elements and compounds in the powdered form. Such a design allows the weld deposits to have the required chemistry without impeding the manufacturing of the consumable electrodes. Tubular electrodes, such as metal-cored and flux-cored electrodes, have also been used in SAW for specialty alloys that are too difficult to draw as a solid wire to the size which is appropriate for the SAW process. For example, hard surfacing applications require the addition of special elements for wear resistance and impact abrasion. Nevertheless, it is attractive to use tubular electrodes in the SAW process to increase the welding deposition rates and control the weld chemistry by selecting the appropriate chemistry of the wire electrode.

[0004] The main ingredients in both metal-cored and flux-cored wires are powdered ferro-alloys. In addition, flux-cored electrodes contain non-metallic compounds to help stabilize the arc and create a desired molten slag composition with such physical properties that allow the molted slag to protect the molten weld metal from various undesirable reagents in the atmosphere. Metal-cored wires typically have no more than 5% of non-metallic compounds and metal oxide powder additions in the core (fill percentage) to help stabilize the arc. Flux-cored electrodes are designed to have non-metallic and metallic oxide ingredients of approximately 20-30% by weight to create the physical slag of desired properties during the welding process.

[0005] Currently the solid wires used in the SAW process work with the granular flux, yielding up to 99% deposition

efficiency. The performance of such welding process is determined mostly by the composition of the granular flux, and much less so by the composition of the wire electrode. Currently, almost 100% of the structural steel market (carbon and HSLA steels) use solid wires. When using flux-cored wire electrodes for SAW, deposition efficiency falls down to about 80%. Welding performance in that case is determined by both the fluxed core of the wire and the granular flux, which turns out to be less efficient.

SUMMARY OF THE INVENTION

[0006] The present invention is a hybrid tubular wire electrode for the SAW process in which not only the external granular flux, but also the composition of the tubular wire itself is a source of the performance oxides. The welding performance is typically controlled by the granular flux: stabilizing the arc and influencing the metal/slag interface, are more controlled by the composition of the core of the hybrid tubular wire. Since the hybrid tubular wire mostly controls the welding parameters, the traditional role of the flux in the SAW process is minimized, meaning that less expensive fluxes can be used without negatively affecting the welding performance and results. The term "hybrid wire" has been chosen to reflect the fact that the tubular wire of the present invention does not fall into the accepted industry categories for either flux-cored or metal cored wires. Metal-cored wires are defined as the ones having less than 5% Wt of non-metallic ingredients. Flux-cored wires are defined as the ones having between about 15% Wt and 30% Wt of non-metallic ingredients.

[0007] The hybrid wire of the present invention comprises approximately 1% Wt to 30% Wt of non-metallic ingredients, with the preferred concentrations selected from the range from about 5% Wt to about 15% Wt. Non-metallic compounds and metallic oxides, which were added to the tubular wires and found to perform well in the SAW process, are CaO , MgO , MgAl , K_2O , CaF_2 , MnO , NaAlF_6 , and K_2AlF_6 . Adding one or more of the listed compounds to the core composition of the tubular wires leads to an improvement of the welding performance in a SAW process due to the properties of core of the wire, while reducing the importance of the granular flux.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1 is a schematic illustration of the submerged arc welding process.

[0009] FIG. 2 is a cross section of the hybrid tubular wire.

[0010] FIG. 3 is a table showing compositions of the tested hybrid tubular wires.

[0011] FIG. 4 is a table showing a composition of the flux.

[0012] FIG. 5 is a table showing steel compositions.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0013] The SAW process is usually operated in an automatic or semi-automatic manner, in which a consumable wire electrode is continuously fed from a reel or spool to a welding gun. The welding gun travels with a predetermined speed along a metal work piece having a granular flux already deposited on the surface of the metal pieces. The

granular flux can be deposited on the work piece before the beginning of the SAW operation or it can be fed through a nozzle of a hopper or a flux tank coupled to the welding gun and deposited during the welding process.

[0014] During the SAW process the heat generated by arc 26 and the tip of consumable electrode 20 melts flux 14 as welding gun 22 and electrode 20 move along metal work piece 12, as it can be seen in FIG. 1. In the SAW process a power source 28 is connected to metal piece 12 and electrode 20. DC or AC can be used for submerged arc welding with the welding currents in the range from 500 to 1500 Amperes. The tip of electrode 20 and arc 26 are shielded by unfused flux 14. The flux deposited on the surface of the metal work piece usually contains deoxidizers and other compounds helping to remove impurities from the molten metal and introduce alloying elements and compounds into the weld. As the electrode submerged in the flux moves along the metal work piece, the flux melts, forms molten flux 16, and rises above the molten metal 18 to form a slag. Consumable wire electrode 20 is fed to the welding gun from reel 24, as shown in FIG. 1. The weld metal usually has a higher freezing temperature and solidifies before the molten slag, which remains molten for a longer time. The molten slag covers the solidified weld metal as a protective layer until the weld metal further cools and becomes less reactive. When the weld metal becomes solid (shown as 10 in FIG. 1) and sufficiently cool, the unmelted flux and the slag are removed from the weld. Base metals which are weldable by the SAW process comprise wrought iron, low carbon steels, low alloy steels, stainless steels, and possibly high and medium carbon, and alloys steels. The compositions of the test wires presented in Table 1 of FIG. 3 are well balanced for welding carbon steels. Examples of the chemistries of the carbon and low alloy steels that can be welded by the hybrid electrode of the present invention are shown as Table 3 in FIG. 5 (in Wt %). The formulations presented in Table 1 can be easily reformulated based on the presented base compositions for welding any HSLA steel using the SAW process.

[0015] A hybrid tubular wire of the present invention for the SAW process comprises a metal sheath 30 and a core 32, as shown in FIG. 2. The core is characterized by a composition of metallic oxides and non-metallic ingredients. The detailed chemical composition of the core of the wire of the present invention is provided in Table 1 shown in FIG. 3. Presented in Table 1 are 10 exemplary compositions with the total percentage of non-metallic compounds ranging from 11% Wt to 30% Wt. It should be noted, though, that the desired effect was observed in the wires with the percentage of non-metallic compounds as low as 1% Wt. The compositions were selected based on the following considerations. When the flux melts, it creates a molten slag which forms a physical barrier between the molten metal of the work piece and the atmosphere (in particular, the nitrogen and oxygen). The difficulty in selecting the appropriate composition of the wire, and especially the core composition, is in coming up with such molten slag system that is sufficiently viscous and, at the same time, sufficiently liquid for the purpose of the SAW process. In particular, on the one hand, the molten slag should be viscous enough to remain above the molten metal of the work piece and not drop off the weld piece, as it could be the case if the molten slag were too liquid. On the other hand, the molten slag shouldn't be too viscous to prevent degazation of the molten pool of metal below the molten slag. Also, careful consideration has been given to the properties of the slag/metal interface to achieve the desired ease of removing the slag from the weld after the SAW

process is complete and the slag and the work piece have solidified and cooled down. To achieve the desired property of the slag/metal interface, the composition of the slag (and, consequently, the core composition of the tubular wire), should be such that the molten slag should have a higher solidification temperature than that of the molten metal of the work piece. If the slag stays molten longer than the metal of the work piece, the weld bead has a better appearance. Also, there needs to be a sufficient difference between the coefficients of thermal expansion of the slag and the metal of the work piece to allow the solid slag to be easily removed from the solid weld.

[0016] The compositions of the tubular wires presented in Table 1 of FIG. 3 were selected to achieve the above-described properties of the slag and the molten metal of the work piece, with the goal of using the chemistry of the wires to enhance the performance of those wires, therefore, enhancing the performance of the wire/flux combination in the SAW process. The non-metallic compounds and metallic oxides added to the core compositions were Al_2O_3 , Al_2O_3 with Na_2O_3 , MgCO_3 , MgAl , CaF_2 , CaCO_3 , CaF_2 , MgO . Table 2 in FIG. 4 presents the composition of the flux which was used in the test weld runs with the test wire compositions. As the test weld runs demonstrated, wire composition 047N-03-001 exhibited the best performance. The release of the slag was the easiest and the fastest over a solid non-tubular wire at the same amperage.

[0017] The process of manufacturing a tubular wire of the present invention involves a series of steps in which a strip (or a sheath material) is fed through the shaping dies which bend the strip and form it into a shape that can later be filled with the ingredients of the core composition. Usually, the shape is a U-shape. The shaped sheath is then filled with the core composition which has a combination of non-metallic compounds and metallic oxides, such as Al_2O_3 , Al_2O_3 with Na_2O_3 , MgCO_3 , MgAl , CaF_2 , CaCO_3 , CaF_2 , MgO . The wire then travels through the closing dies which close it into a tubular form in which the sheath completely encapsulates the core, forming a cored wire as illustrated in FIG. 2. The ingredients of the core composition are often powdered, which powder becomes compacted when the encapsulated wire is fed through the drawing dies to reduce the wire's diameter to the final desired size.

[0018] A welding apparatus for the SAW process utilizing the tubular wire of present invention is shown as an illustrative example in FIG. 1. The welding apparatus comprises power supply 28 (AC or DC), welding gun 22 with electrode 20 and means 24 for feeding the electrode into the welding gun. An example of the means 24 for feeding the electrode shown in FIG. 1 is a wire drive and a wire reel 22. It should be understood, of course, that any other way of feeding the wire electrode into the welding gun falls within the scope and spirit of the present invention. Granular flux 14 is provided on the surface of welding work piece 10 either through a nozzle connected to the welding gun or independently before the beginning of the SAW welding process. One possible flux composition is provided in Table 2 of FIG. 4. Electrode 20 has a sheath and a core characterized by a core composition comprising non-metallic compounds and metallic oxides in accordance with the compositions as shown in Table 1 of FIG. 3. The power source supplies AC or DC current to the electrode and the arc is formed between the wire electrode 20 and the work piece 12 as shown in FIG. 1, providing the heat necessary for melting flux 14 and the tip of wire electrode 20.

[0019] To form a weld on a work piece using the SAW apparatus with a novel hybrid tubular wire electrode of the present invention, a welding process uses a welding apparatus with means for feeding the wire electrode and means for supplying a flux on the surface of the work piece. The means for feeding the wire into the welding apparatus can comprise a wire drive and a wire reel, or any other suitable arrangement supplying the wire into the apparatus with the speed sufficient to replace the portion of the wire consumed during the SAW process. It is contemplated that the means for feeding the wire into the welding apparatus can be internal or be located outside of the apparatus. The welding apparatus is coupled to a DC or AC power supply and the arc is formed between the electrode and the work piece on which the weld is to be formed. Feeding the hybrid tubular wire electrode of the present invention into the welding apparatus involves providing the wire with a sheath and a core having a core composition comprising one or more compounds selected from the group consisting of Al_2O_3 , Al_2O_3 with Na_2O_3 , MgCO_3 , MgAl , CaF_2 , CaCO_3 , CaF_2 , MgO . The welding gun moves along the work piece, as shown by the direction of travel in FIG. 1, while wire electrode 20 is submerged in flux 14. Flux 14 is typically deposited onto the surface of the work pieces either before the beginning of the SAW process or during the welding process. If the flux is deposited onto the work pieces during the welding process, it is usually done via a nozzle connected to the welding gun. As welding gun 22 moves along work piece 12, the heat generated by arc 26 melts the tip of wire electrode 22 and the granular flux around the tip of the electrode, forming the pool of molten metal 16 of work piece 12 below the pool of molten slag 18. As the welding gun moves along its direction of travel, solidified weld metal 10 forms the weld. Molten slag 16 also solidifies and is later removed from the weld.

[0020] It has been, therefore, demonstrated that an addition of one or more specified non-metallic ingredients from the range of 1% Wt to 30% Wt to the core of a tubular wire electrode formulated for the SAW process improves the welding performance due the properties of the core. The written description of the invention enables one skilled in the art to make and use what is at present considered to be the best mode of the invention, and it should be appreciated and understood by those skilled in the art that the existence of variations, combinations, modifications and equivalents falls within the spirit and scope of the specific exemplary embodiments disclosed herein. It is also to be understood that the illustrative examples described herein are not to be construed as limiting the present invention in any way. The objects, features and advantages of the present invention as claimed in the appended claims are applicable to all types of metal core wires, such as low carbon metal core, stainless steel metal core and low alloy metal core wires.

What is claimed is:

1. A welding apparatus for a submerged arc welding process comprising:

a welding gun having means for feeding a tubular electrode into the welding gun; and

the tubular electrode formulated for use in the submerged arc welding process and having a sheath encapsulating a core with a composition selected from the group of non-metallic compounds consisting of Al_2O_3 , Na_2O_3 , MgCO_3 , MgAl , CaF_2 , CaCO_3 , CaF_2 , MgO and combinations thereof, wherein the total percentage of one

or more non-metallic compounds in the core composition ranges from about 1% Wt to about 30% Wt.

2. The welding apparatus as in claim 1, wherein the total percentage of one or more non-metallic compounds ranges between 5% Wt and 15% Wt.

3. The welding apparatus of claim 1, wherein the non-metallic compounds are Al_2O_3 and Na_2O_3 with the total percentage of 14% Wt.

4. The welding apparatus of claim 1, wherein the means for feeding the tubular electrode into the welding gun comprise a wire drive and a wire reel.

5. A submerged arc welding process comprising:

providing a submerged arc welding apparatus with means for feeding an tubular electrode into the welding apparatus;

depositing a flux onto a work piece;

submerging the tubular electrode into the flux;

forming an arc between the tubular electrode and the work piece by coupling the submerged arc welding apparatus to a power source;

feeding the tubular electrode into the welding apparatus, the tubular electrode having a sheath encapsulating a core with a composition selected from the group of non-metallic compounds consisting of Al_2O_3 , Na_2O_3 , MgCO_3 , MgAl , CaF_2 , CaCO_3 , CaF_2 , MgO and combinations thereof, wherein the total percentage of one or more non-metallic compounds in the core composition ranges from about 1% Wt to about 30% Wt; and

forming a weld on the work piece by melting the work piece, the flux and the tip of the tubular electrode using the heat generated by the arc.

6. The method of claim 5, further comprising moving the welding apparatus along the work piece.

7. The method of claim 5, wherein the work piece is a carbon steel.

8. The method of claim 5, wherein the total percentage of one or more non-metallic compounds ranges between 5% Wt and 15% Wt.

9. The method of claim 5, wherein the non-metallic compounds are Al_2O_3 and Na_2O_3 with the total percentage of 14% Wt.

10. A tubular weld wire comprising:

a steel sheath encapsulating a core;

the core formulated for submerged arc welding and comprising one or more non-metallic compounds selected from the group of non-metallic compounds consisting of Al_2O_3 , Na_2O_3 , MgCO_3 , MgAl , CaF_2 , CaCO_3 , CaF_2 , MgO and combinations thereof, wherein the total percentage of one or more non-metallic compounds in the core composition ranges from about 1% Wt to about 30% Wt.

11. The tubular weld wire of claim 10, wherein the core composition further comprises compacted Fe, FeMg, and FeSi.

12. The tubular weld wire of claim 10, wherein the total percentage of one or more non-metallic compounds ranges between 5% Wt and 15% Wt.

13. The tubular weld wire of claim 10, wherein the non-metallic compounds are Al_2O_3 and Na_2O_3 with the total percentage of 14% Wt.

14. A welding apparatus for a submerged arc welding process comprising:

a welding gun having means for feeding a tubular electrode into the welding gun; and the tubular electrode formulated for welding low carbon steels with a percentage of C being up to 0.15% in the submerged arc welding process and having a sheath encapsulating a core with a composition selected from the group of non-metallic compounds consisting of Al_2O_3 , Na_2O_3 , MgCO_3 , MgAl , CaF_2 , CaCO_3 , CaF_2 , MgO and combinations thereof, wherein the total percentage of one or more non-metallic compounds in the core composition ranges from about 1% Wt to about 30% Wt.

15. The welding apparatus of claim 14, wherein the tubular electrode is also formulated for welding low alloy steels with a percentage of C being up to 0.15% in the submerged arc welding process.

16. The welding apparatus of claim 14, wherein the total percentage of one or more non-metallic compounds ranges between 5% Wt and 15% Wt.

17. The welding apparatus of claim 15, wherein the total percentage of one or more non-metallic compounds ranges between 5% Wt and 15% Wt.

18. A submerged arc welding process comprising:

providing a submerged arc welding apparatus with means for feeding an tubular electrode into the welding apparatus;

depositing a flux onto a work piece of low carbon steel or low alloy steel with a percentage of C being up to 0.15%;

submerging the tubular electrode into the flux;

forming an arc between the tubular electrode and the work piece by coupling the submerged arc welding apparatus to a power source;

feeding the tubular electrode into the welding apparatus, the tubular electrode having a sheath encapsulating a core with a composition selected from the group of non-metallic compounds consisting of Al_2O_3 , Na_2O_3 , MgCO_3 , MgAl , CaF_2 , CaCO_3 , CaF_2 , MgO and combinations thereof, wherein the total percentage of one or more non-metallic compounds in the core composition ranges from about 1% Wt to about 30% Wt; and

forming a weld on the work piece by melting the work piece, the flux and the tip of the tubular electrode using the heat generated by the arc.

19. The method of claim 18, wherein the total percentage of one or more non-metallic compounds ranges between 5% Wt and 15% Wt.

20. The method of claim 18, wherein the non-metallic compounds are Al_2O_3 and Na_2O_3 with the total percentage of 14% Wt.

* * * * *

[54] WELDING METHOD AND MATERIALS

117/202, 203, 204, 205, 206; 148/24, 26

[75] Inventors: Haruyoshi Suzuki, Seki; Thuyoshi Takino, Yachio; Naomichi Mori, Machida; Isao Sugioka, Funabashi; Osamu Matsuda, Narashino; Shozo Sekino, Kitakyushu; Hiroyuki Honma, Utsunomiya, all of Japan

[56]

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[73] Assignees: Nippon Steel Corporation; Nippon Steel Welding Products Engineering Co., Ltd., both of Tokyo, Japan

[22] Filed: Sept. 14, 1973

[21] Appl. No.: 397,329

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 169,915, Aug. 9, 1971, abandoned.

Primary Examiner—J. V. Truhe

Assistant Examiner—G. R. Peterson

Attorney, Agent, or Firm—Toren, McGeedy and Stanger

[30] Foreign Application Priority Data

Sept. 29, 1970 Japan..... 45-84613
Aug. 14, 1970 Japan..... 45-75575
Dec. 10, 1970 Japan..... 45-109847

[57]

ABSTRACT

Methods and materials for submerged arc welding for obtaining a high toughness welded metal containing titanium and boron by using a flux cored wire composed of a steel sheath and a core containing titanium and boron with the addition of a metal fluoride.

3 Claims, 7 Drawing Figures

[52] U.S. Cl. 219/73; 219/146; 117/205
[51] Int. Cl. B23K 9/18
[58] Field of Search 219/73, 146, 145, 137;

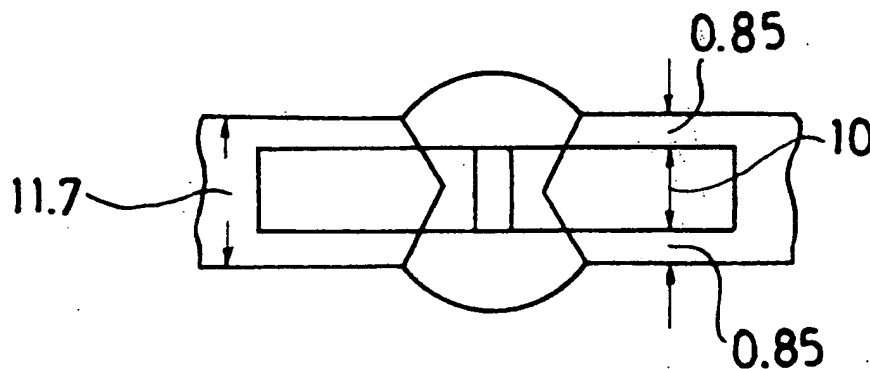


FIG. 1

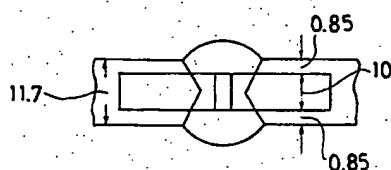
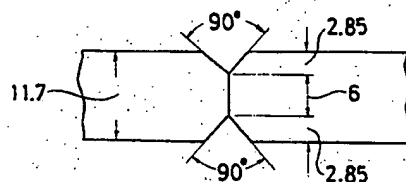


FIG. 2



INVENTORS

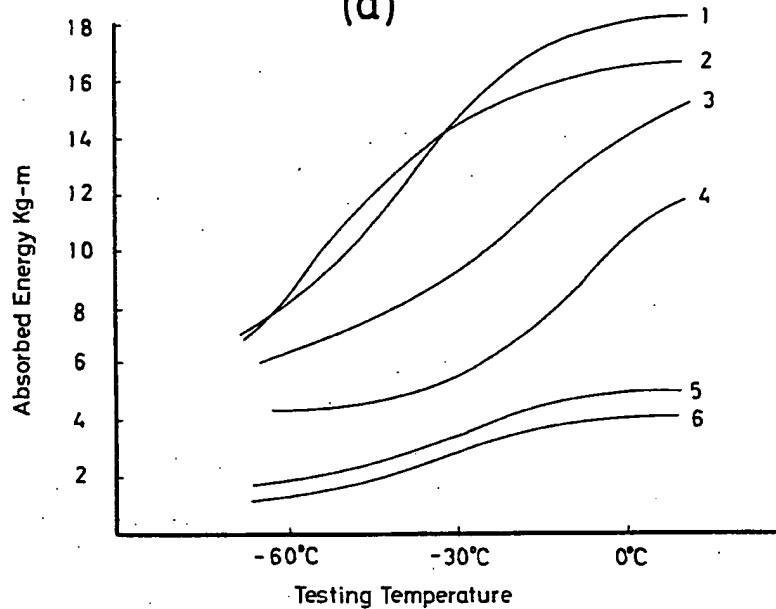
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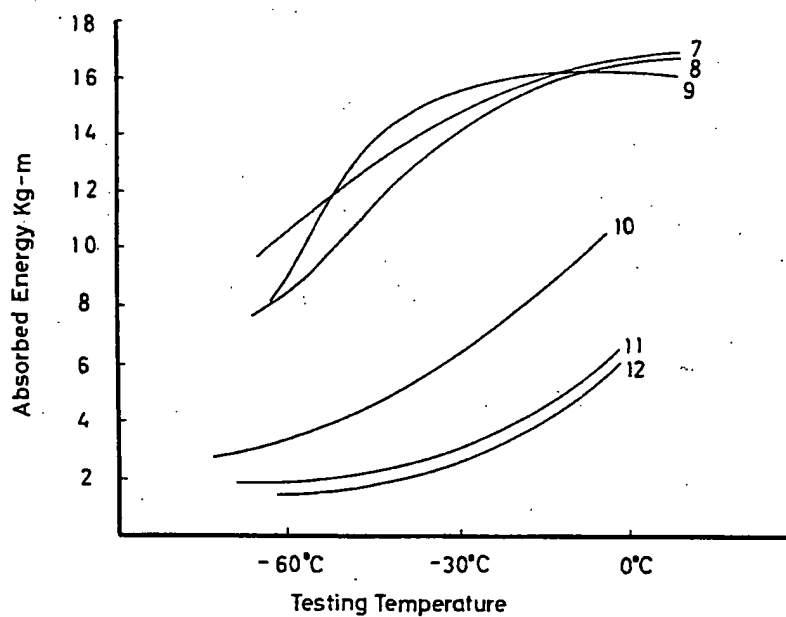
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FIG. 3

(a)



(b)



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FIG. 4
(a)

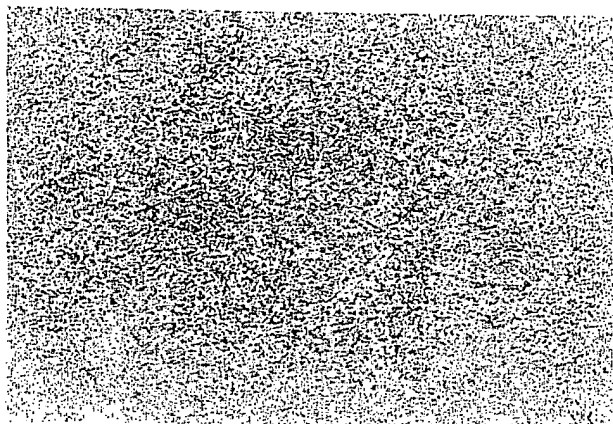


FIG. 4
(b)

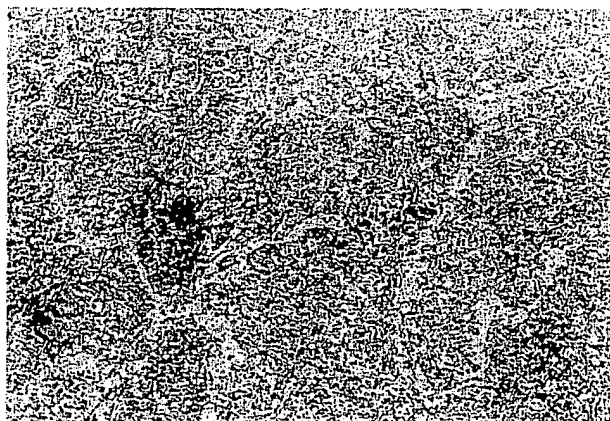
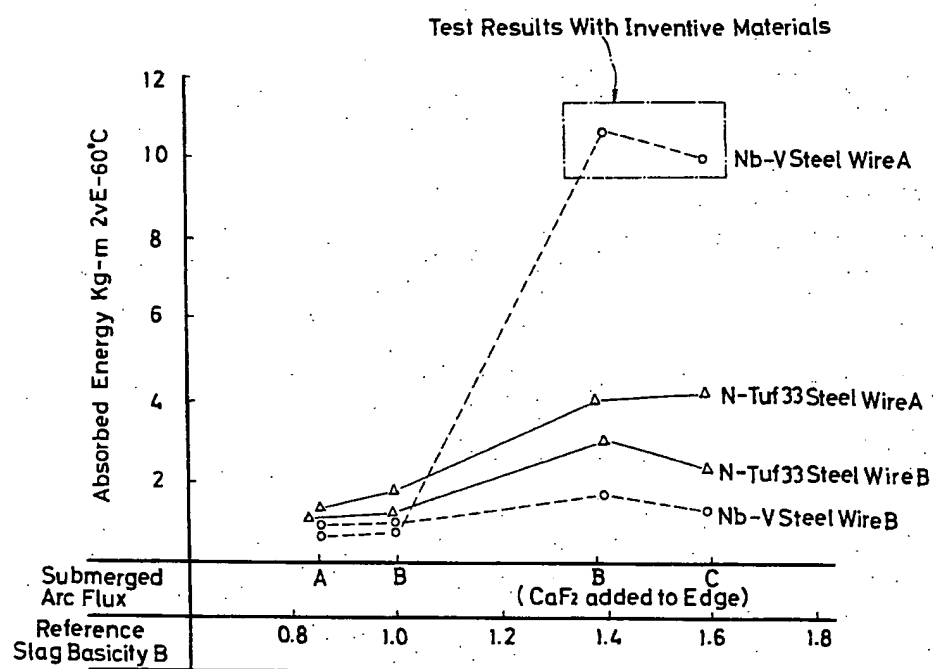


FIG. 5



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WELDING METHOD AND MATERIALS

CROSS REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of copending application Ser. No. 169,915, filed Aug. 9, 1971, now abandoned, the contents of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to methods and materials for submerged arc welding for obtaining a high toughness welded metal containing titanium and boron by using a flux cored wire containing titanium and boron with the addition of a metal fluoride.

This invention also relates to a method of submerged arc welding to obtain a welded metal with high toughness by one layer welding on both sides or a small layer heap welding, as well as welding materials and a filled-up wire for the submerged arc welding use thereof.

2. Description of the Prior Art

For the welded part of a steel for low temperature use, such as, aluminum refined killed steel and 2.5 Ni-steel used for LPG freighter and other uses, the low-temperature impact value at about -60°C is an important property. These steel sheets are usually used with a thickness of about 6–20 mm, and in order to join flat plates to one another, it is desirable to adopt an automatic submerged arc welding to increase the welding efficiency. However, with the conventional combination of a submerged arc flux and wire, satisfactory low-temperature impact value cannot be obtained with a high efficiency welding method, e.g. submerged arc welding, i.e. welding with a relatively large electric current (or heat input) or one layer welding on both sides. A welded metal with high toughness can only be obtained by lowering the heat input or by a large heap welding at the sacrifice of the efficiency.

Various attempts have been made to increase the impact value of the welded metal by a single layer or one layer on both sides submerged arc welding. It has been considered in general that a welded metal with high toughness can be obtained when the O_2 content (oxide inclusions) in the welded metal is reduced by increasing the basicity of the flux or when an alloy element, such as, Ni and Mo is added. Typically, up to 3.5% by weight Ni and up to 0.8% by weight Mo are added.

However, when a highly basic submerged arc flux is used, there is a tendency to increase the grain size of the ferrite crystals in the microscopic structure of the welded metal, resulting in the degradation of the impact value as compared with the case when a neutral submerged arc flux is used.

On the other hand, although it is well known that the impact value of the welded metal by a single layer— or a small layer heap welding can be increased by using a neutral submerged arc flux containing a large amount of metal fluoride such as CaF_2 , it is difficult to obtain a sufficiently high impact value, for instance NK standard value (KS TAWS, more than 35 kg-m) at a low temperature of about -60°C .

SUMMARY OF THE INVENTION

One of the objects of this invention is to offer a flux cored wire for submerged arc welding in which a fluoride or metal having a low vapor pressure is added to-

gether with titanium and boron. The essential point thereof is a flux cored wire for submerged arc welding in which CaF_2 , which shows a vapor pressure of 1 atmospheric pressure at 2500°C , other fluorides more volatile, such as, NaF, LiF, KF, MgF_2 , MnF_2 , K_2ZrF_6 , Na_2ZrF_6 , K_2TiF_6 and Na_2TiF_6 .

Particularly the flux cored wire of the present invention is composed of a hollow mild steel sheath having a core composed of about 0.04 to 1.0% titanium, about 0.002 to 0.05% boron and about 4 to 25% of a fluoride selected from the group consisting of CaF_2 , NaF , KF, LiF , MgF_2 , and MnF_2 , all percentages being by weight based on the total weight of the electrode, the balance of the weight of the electrode being the steel sheath.

The present invention also comprises a method for submerged arc welding to obtain a weld having a high toughness by using a submerged arc welding flux having a basicity (as defined hereinafter) in the range from about 0.90 to 1.30, in conjunction with the above defined flux cored wire.

When such a fluoride with high vapor pressure is added in the wire, a wide space in the arc void is sealed with the vapor thereof, the oxidation and nitrogenation of titanium is prevented, the amount of MnO and manganese silicate which have an influence on the decrease of the amount of O_2 and particularly on the deterioration of the toughness are diminished remarkably, and the oxidation and nitrogenation of boron is also diminished. Thus, it is possible to maximize the effect of the coexistence of titanium and boron on the improvement of the hardenability.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an explanatory drawing showing the position where the impact test piece is taken.

FIG. 2 is a drawing to show the shape of the welding notch.

FIG. 3(a) and (b) are the graphs showing the transition curve of the examples of this invention and of the comparison examples.

FIG. 4(a) and (b) are the microscopic photographs of the welded metal of the test pieces in the examples of this invention and in the comparison examples.

FIG. 5 is a graph showing the absorption energy values of the welded metal in the examples of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

It is well known that the toughness of welded metal changes remarkably not only by the compositions of the master steel sheet and the welding materials, which determine the composition of the welded metal, but also by the composition of the flux.

Generally speaking, when the basicity of the flux is high, while O_2 content in the welded metal is diminished and the toughness is improved, defects are encountered, e.g. the peeling of the slag becomes difficult, the appearance of the bead is worse and the workability becomes inferior, for instance, the undercut is formed easily.

Moreover, when the basicity is high, H_2 content in the welded metal is increased, which can produce pits, blowholes and weld cracks.

As for the method of submerged arc welding to obtain a welded metal with high toughness without losing the workability, it is advantageous to carry out the welding by combining a flux cored wire in which a flux

agent is filled in the hoop material with a submerged flux. The reason is as follows: since the flux cored wire is exposed to an arc atmosphere at very high temperature, the chemical reaction expected to occur between the flux and the molten steel reaches equilibrium in a very short period, and consequently the influence of the flux charged in the edges becomes secondary; thus, while the basicity of the slag, as seen as a whole, is relatively low, it is possible to obtain nevertheless a welded metal with high toughness.

It is a further merit of using flux cored wire that a tolerable amount of alloy component can be added in the hoop as a cored material, and more advantageously a sufficient amount of deoxidizing and denitrogenizing agent can directly be added. In using a solid wire, the addition of alloy components, deoxidizing and denitrogenizing agents, etc., is restricted owing to the problem occurring in melting and in hot rolling.

As a result of various investigations on the controlling factors on the toughness of welded metal in the welding of 50-80 kg/mm² class high tension steel and of steels for low temperature use, the present inventors found that the influence of proeutectoid ferrite formed along the γ -grain boundary on the fracture transition temperature (T_m) is very great, while the influence of cleanliness, particularly MnO in the inclusion determines the vE shelf energy. The reason why proeutectoid ferrite deteriorates the toughness is due to the facts that, when proeutectoid ferrite deposits, high carbon bainite or acicular high carbon martensite is formed around it, and as they are brittle, they become the origin or the propagation path of the formation of cracks, and since the proeutectoid ferrite crystals are large, cracks propagate through the grains at once.

Therefore, in order to improve the toughness of welded metal, it is advisable to prevent the formation of proeutectoid ferrite by elevating the hardenability.

However, it is undesirable to elevate the hardenability by increasing the carbon equivalent, because the strength becomes too high, causing an unbalance in strength with the master steel and forming cracks.

Boron is effective to improve the hardenability (to retard the deposition of proeutectoid ferrite) without increasing the strength excessively. While only a small amount of boron is effective, it is necessary that it is segregated along γ -grain boundary during $\gamma \rightarrow \alpha$ transformation. Boron has no effect when it is dispersed in γ -grains as a nitride or oxide. Therefore, it is necessary to protect the boron from nitrogenation and oxidation.

For this purpose, the addition of an element having a

oxidation than Zr. The solubility of Ti in iron is large, easily forming a solid solution as the γ -phase, and Ti itself can improve the hardenability, while Zr is very easily consumed by oxidation, has a low solubility in iron, forming almost no solid solution as the γ -phase, and thus does not increase the hardenability.

When Ti alone is added in the flux cored wire, Ti is oxidized out in passing the arc void, and the effect of improving the hardenability as in the coexistence with boron cannot be expected. It is important to protect Ti from oxidation and nitrogenation and to let the Ti reach the melting pond by evaporating volatile metals, e.g., fluorides or chlorides in the arc void to expel oxygen and nitrogen in the air or which come from the flux, and which invade into the arc void under ordinary conditions.

Although the idea of using a vapor of fluoride for sealing is similar to the case of the flux cored wire for use in open arc (nongaseous arc) welding, as compared with the case of open arc welding in which the arc is exposed to open air and the sealing effect is very insufficient; the use submerged arc welding, in which the sealing effect is complete and the Ti can be protected effectively, has great merit.

When Ti reaches the melting pond without suffering oxidation and nitrogenation, Ti forms oxides and other components prior to the Mn and Si at the surface of the melting pond facing the arc void, and migrates to the slag layer, and consequently the oxygen content in the molten steel is lowered, SiO₂ and MnO components in the inclusion are diminished, and the cleanness is improved. Moreover, by the synergistic effect with boron, the effect of Ti is doubled.

Another object of the present invention is to offer a method of submerged arc welding to obtain a welded metal with high toughness characterized in which a flux with nearly neutral composition, whose basicity b expressed by the Formula (b) shown hereinafter lies in the range 0.90-1.30, is used as a submerged arc flux and a flux cored wire containing one or more than one component selected from a slag-forming agent, an arc stabilizer, a deoxidizer or denitrifier, alloy elements and iron powder as a cored material is used as a submerged arc wire are used in combination. It is a necessary condition for the wire that the contents of metal fluorides, Ti and B in the cored material to the total weight of the wire are respectively in the range mentioned below.

Contents of metal fluoride, Ti and B in the flux cored wire:

Metal fluoride (CaF ₂ , NaF, MgF ₂ , etc.)	4 - 25%
Ti	0.04 - 1.0%
B	0.002 - 0.5%

$$\text{Basicity } b = \frac{\text{CaO} + \text{MgO} + \text{BaO} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Li}_2\text{O} + \text{CaF}_2 + \frac{1}{2}(\text{MnO} + \text{FeO})}{\text{SiO}_2 + \frac{1}{2}(\text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{ZrO}_2)} \quad (\text{wt.}\%)$$

Formula (1)

strong affinity with oxygen and nitrogen, such as, Al, Ti and Zr is necessary.

By investigating by experiments the influence of each of these elements, it has been proved that boron alone and Zr + B has entirely no effect, the effect of Al + B is insufficient, and Ti + B is most effective.

Why Ti is effective while Zr has no effect may be due to the reasons that Ti is more slowly consumed by

Said submerged arc flux may naturally contain minute amounts of oxide and other compounds as impurities besides the components in Formula (1).

In Formula (1), CaF₂ is calculated as a basic component. This is because fluoride serves to reduce practically the contents of O₂ and S in the deposit, and may be considered to have an effect similar to the basic components CaO, MgO, etc.

5

Only when the above mentioned conditions are satisfied, can a welded metal with high toughness be obtained without or with the addition of only a small amount of such elements as Mo and Ni, which are generally considered to be effective for the improvement of the toughness.

Particularly, it becomes possible to obtain a welded metal with high low-temperature impact value without the addition of Mo, which is added generally to obtain a welded metal with high toughness in a single layer—or a small layer heap welding.

One characteristic of this invention is to combine a submerged arc flux with a neutral composition, having excellent welding workability, with a flux cored wire containing CaF_2 .

A highly basic flux generally is disadvantageous since its welding workability (the resistance against pit formation and the appearance of bead) is inferior, and the range of the welding condition is very limited. On the other hand, as a neutral flux is used in this invention, its welding workability is excellent, and this invention gives a welded metal with a better impact value than in the case when a filled-up flux wire containing B and Ti at the same time is combined with a highly basic flux.

The reason may closely relate to the fact that the N_2 content in the welded metal is reduced more by using a neutral flux than in the case when highly basic flux is used, and it seems that the effect of B and Ti in reducing the N_2 content is particularly remarkable in the combination of a neutral flux with a wire containing CaF_2 .

When the submerged arc flux becomes acidic in the range such that its basicity is lower than 0.9, the O_2 content in the welded metal becomes high and the addition of B and Ti has no particular effect on the improvement of the impact value. When its basicity becomes greater than 1.30, the workability becomes worse as above mentioned, for instance, the tendency of pit formation is observed.

An important characteristic of the present invention is the use of a filled-up wire. The addition of CaF_2 in the submerged arc flux is generally very difficult, because the addition makes the welding workability inferior. On the other hand, the addition of CaF_2 in the wire has no serious influence on the welding workability. Moreover, the addition of B in the wire is the most suitable method for the addition of B in the welded metal.

Namely, in order to add a suitable amount of B in the welded metal, considerable B is lost during the reaction at the arc and in the melting pond, and its remaining percentage in the welded metal becomes fairly low. Therefore, to supply B in a solid wire, a fairly large amount of B should be added in the wire.

It has well been known that, when more than 0.01% of B is added in the solid wire, the working becomes difficult in the wire drawing and particularly in the hot rolling.

By the use of a filled-up wire, however, it is possible to add a definite amount of B easily in the form of pellet or powder as an alloy element in the filling material. Its merit is obvious.

As Ti and B in the wire are consumed by oxidation, nitrification, etc. during welding, the lower limits of B and Ti contents are respectively 0.4% and 0.002%. Below these limits, almost none will remain in the welded metal, and no improvement in the impact value can be observed. While up to about 1.0% of Ti improves the impact value, the addition of more than this value increases the hardness of the welded metal and

6

has a tendency to decrease the impact value. When more than 0.05% of B is added, the welded metal contains more than about 0.01% of B, decreasing the impact value and at the same time forming heat cracks. Accordingly, 0.04–1.0% of Ti and 0.002–0.05% of B are the effective ranges.

As for the amounts of metal fluoride (CaF_2 , NaF , MgF_2 , etc.) to be added to the flux cored wire, below 4% has no distinct effect and the addition of more than 25% injures the arc stability and makes the welding impossible.

To add Ti and B at the same time in the flux cored wire is another characteristic of this invention. After various experiments, it was ascertained that, in the submerged arc welding, the synergistic effect can not be obtained in the combination Ti — Zr, Ti — Al, Ti — V, B — Zr, B — Al, B — V and others.

It is found further that the addition of such elements as Al, V and Nb together with Ti and B improves the impact value still more.

As above mentioned, it is characteristic of this invention that a welded metal with high toughness can only be obtained when a submerged arc flux with a neutral composition, whose basicity b lies in the range 0.90–1.30, is combined with a filled-up wire, in which it is a necessary condition that metal fluoride, such as, CaF_2 , Ti and B are contained at the same time in the range as above mentioned. When any of these conditions is lacking, a satisfactory result cannot be obtained.

To compare the microstructure of the welded metal of this invention with that of other welded metals, it is observed that proeutectoid ferrites at the austenite grain boundary diminish remarkably, and ferrite crystals in the grain become very fine. This property may be the reason why high toughness can be obtained. In the welded metals without the scope of this invention, coarse proeutectoid ferrites at the grain boundary or acicular ferrites are observed, and the toughness is low.

It is considered that the reason why proeutectoid ferrites diminish remarkably and ferrite crystals in the grain become very fine when Ti and B are added at the same time, the submerged arc flux is neutral, and a suitable amount of metal fluoride is contained in the wire, is due first of all to the existing state of boron in the welded metal, i.e., whether or not B exists as a solid solution, and that boron in the solid solution controls the formation of ferrite nuclei at the transformation of austenite. The formation of ferrite nuclei may be controlled still more in this invention as the N_2 content is reduced by the use of a neutral flux, the O_2 content is reduced by the addition of CaF_2 , and Ti is present. Thus, the present invention provides various necessary conditions effective for the formation of fine ferrite crystals. Further, as a method to accomplish this object, it is a necessary condition that the submerged arc wire is a filled-up wire.

This invention is advantageous to obtain a submerged arc welding material suitable for the range of Nb–V (giving high impact toughness).

In welding a steel containing Nb (V) by the use of conventional submerged arc welding material, the impact toughness values of the welded metal becomes considerably low as compared with the case of usual steel containing no Nb (V). On the other hand, the welding material of this invention produces a welded metal with a rather high toughness in the case of Nb (V) steel.

Particularly, the material of this invention exhibits its feature when Nb (V) steel is welded by a single layer—or a small heap welding.

The following examples illustrate the present invention:

EXAMPLE 1

In this example, a 50 kg/mm² class Si-Mn steel with the components as shown in Table 1 was used as a master steel.

A V-shaped ditch was cut in the steel sheet, a submerged arc flux containing SiO₂, CaO, MnO and others as shown in Table 2 was sprinkled therein, and welded

clusions, and a low content of Ti. To examine the structure thereof, a large quantity of proeutectoid ferrite was observed. The toughness is worse due to two points: the amount of inclusions and the decreased hardenability. By adding CaF₂, the oxygen content decreases, the amount of remaining Ti is increased, and the toughness is improved remarkably.

When more volatile LiF or NaF is added instead of CaF₂, while the remaining rate of Ti is only slightly improved, the oxygen content is reduced still more. As a result, as compared with the case of CaF₂, the toughness of the welded metal together with $\sigma_{T_{ss}}$ and $\sigma_{E_{shelf}}$ is improved still more.

Table 4

	Analytical result, cleanness and mechanical properties(%)									
	O	Analytical Result N	Result MnO	sol Ti	Clean-ness(%)	(°C) $\sigma_{T_{ss}}$	(kg-m) σ_{E-40}	(kg-m) $\sigma_{E_{shelf}}$	(kg/mm ²) Ts	
A	0.040	0.0074	0.033	0.024	0.133	-30	5.2	15	53.8	
B	0.058	0.0075	0.051	0.020	0.156	-15	2.0	9	54.0	
C	0.040	0.0070	0.026	0.024	0.121	-27	4.3	16	53.2	
D	0.035	0.0068	0.024	0.028	0.110	-36	6.8	20	53.0	
E	0.083	0.0052	0.084	0.005	0.340	20	1.3	7	53.2	

on both sides by using a flux cored wire. Charpy test was made for the welded metal obtained.

The weight of hoop material in the total weight of the flux cored wire was about 75-80%, the remainder being the filling material. The rates of cored materials were as shown in Table 3. Wires A and B contain CaF₂, and C, D and E contain respectively LiF, NaF and Ca-Si. F is a standard wire containing no special additive.

Analytical results of oxygen, nitrogen, inclusion and soluble Ti, cleanliness, and mechanical properties — $\sigma_{T_{ss}}$, σ_{E-40} , (absorbed energy at -40°C in a 2 mm V-notch Charpy Impact Test), $\sigma_{E_{shelf}}$ (shelf energy in 2 mm V-notch Charpy Impact Test) and Ts (tensile strength) of the welded metal obtained in the welding with the use of a filled-up wire are shown in Table 4.

Table 1

Chemical components in the master sheet (%)				
C	Si	Mn	Ni	Al
0.08	0.27	1.28	0.01	0.023

Table 2

Composition of flux for submerged arc welding (%)				
SiO ₂	CaO	MnO	CaF ₂	Others
42	17	20	8	balance

Table 3

	Mo	Ti	B	Rate of filling materials in the filled-up wire (%)				Iron Powder	Ni Powder	Mn Powder	Fe-Si Powder	LiF
				CaF ₂	NaF	Ca-Si						
A	0.3	0.2	0.005	10	—	—		10	2.5	1.5	0.2	—
B	"	"	"	5	—	—		5	"	"	"	—
C	"	"	"	—	—	—		6	"	"	"	5
D	"	"	"	—	5	—		6	"	"	"	—
E	"	"	"	—	—	—		25	"	"	"	—

*Balance - Carbon Steel Sheath

As it is clear from the results, in the case of filled-up wire F containing no special additive, such as, fluoride, the welded metal has high contents of oxygen and in-

clusions, and a low content of Ti. To examine the structure thereof, a large quantity of proeutectoid ferrite was observed. The toughness is worse due to two points: the amount of inclusions and the decreased hardenability. By adding CaF₂, the oxygen content decreases, the amount of remaining Ti is increased, and the toughness is improved remarkably.

When more volatile LiF or NaF is added instead of CaF₂, while the remaining rate of Ti is only slightly improved, the oxygen content is reduced still more. As a result, as compared with the case of CaF₂, the toughness of the welded metal together with $\sigma_{T_{ss}}$ and $\sigma_{E_{shelf}}$ is improved still more.

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without saying that, besides the necessary components to constitute the invention, such as, various fluorides, composite fluorides, Ti and B, such supplementary agents as an arc stabilizer comprising various oxides and carbonates, a slag-forming agent, a deoxidizer comprising Fe—Si, Fe—Mn and others, an alloying element and iron powder can be added as a filling mate-

The compositions of the submerged arc flux were as shown in Table 7, and those of the submerged arc wire were as in Table 8. Four samples of flux and eight samples of wire were tested under various combinations. Eight combinations, submerged arc flux B, C and filled-up wire A, B, C, D, respectively, belonged to the scope of this invention.

Table 7

Flux	SiO ₂	Chemical composition of submerged arc flux (wt %)							Basicity B
		CaO	MnO	MgO	TiO ₂	Al ₂ O ₃	CaF ₂	Others	
A	50	30	—	7	—	4	5	4	0.81
B*	38	22	10	7	4	8	10	1	1.00
C*	32	22	10	13	4	7	7	5	1.25
D	30	30	—	20	—	10	5	5	1.57

*Flux necessary for this invention.

Table 8

	Electrode Composition								
	(All percentages are by weight based on the weight of the electrode)								
	A	B	C	D	E	F	G	H	I
Calcium fluoride	15	15	12	6	15	15	15	15	—
Magnesium fluoride	—	—	3	—	—	—	—	—	—
Flux for submerged arc welding listed in Table 7	—	—	—	—	—	—	—	—	15
Fe-Si (43% Si)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Mn powder	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Ni powder	1.5	—	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Fe-Mo (60% Mo)	0.75	0.75	—	0.75	0.75	0.75	0.75	0.75	0.75
Fe-Ti (42% Ti)	0.7	0.7	0.7	0.7	—	—	—	0.7	0.7
Fe-Zr (20% Zr)	—	—	—	—	1.4	—	—	—	—
Fe-Al (50% Al)	—	—	—	—	—	0.6	—	—	—
Fe-Boron (20% boron)	0.075	0.075	0.075	0.075	0.075	0.075	0.075	—	0.075
Iron powder	—	—	—	15	—	—	—	—	—
Carbon steel sheath	bal.	bal.	bal.	bal.	bal.	bal.	bal.	bal.	bal.

Electrode diameter: 3.2 mm

rial.

EXAMPLE 2

Aluminum killed steels containing Nb and V with the compositions shown in Table 5 were submerged arc welded one layer on both sides. Experimental results of the impact values of the welded metal obtained will be explained.

The size of the master sheet was: 11.7 mm in thickness, 200 mm in width and 400 mm in length. Notches as in FIG. 2 were made by a mechanical working, and the submerged arc welding was carried out under the condition in Table 6. Impact test pieces were taken at the position shown in FIG. 1.

Table 5

C	Chemical composition of the steel sheet (%)							Iron and impurities
	Si	Mn	P	S	Nb	V	Al	
0.12	0.24	1.27	0.014	0.010	0.03	0.03	0.03	balance

Table 6

Welding condition			
Back side	430 Amp	35 V	45 cm/min.
Upper side	600 Amp	38 V	45 cm/min.

In FIG. 3(a) and (b), experimental results on 2 mm V notch Charpy test of the welded metals obtained by the welding with various combinations are shown with the use of the transition curve between absorption energy and temperature.

Samples for curves 1 and 2, whose combinations are respectively flux C and wire D, and flux B and wire A, and curves 7, 8 and 9, whose combinations are respectively flux B and wire B, flux B and wire A, and flux B and wire C, are inventive examples and show very excellent transition curves. Other curves 3, 4, 5, 6, 10, 11 and 12 are the transition curves for comparison examples, their combinations being respectively flux D and wire D, flux B and wire H, flux B and wire I, flux A and

wire D, flux B and wire F, flux B and wire E, and flux B and wire C.

Among these results, curves 1, 2 and 3 show the influence of the basicity of the flux. It is obvious that, even if the wire satisfies the condition of this invention, the impact value is low when the basicity of the flux is too low (too acidic). Additionally, the welding workability, such as, the appearance and shape of the bead

and resistance against pit formation is worse and the impact values are inferior as compared to the inventive combinations when the basicity is high.

In the sample for curve 4, B is not added in the wire while all other conditions are satisfied, and the impact value is low.

The sample for curve 6 does not satisfy the inventive conditions because CaF_2 is not added in the filled-up wire, and thus, the results show that the impact value is very low even if the other conditions are satisfied.

Curves 7, 8 and 9 belong to the case of the inventive combination, showing that an excellent impact value can be obtained without the addition of Ni and Mo.

Curves 10, 11 and 12 are to show that no high impact value can be obtained when an element other than Ti, for instance, Zr or Al, is used together with B or B is used alone, and the inventive condition being unsatisfied.

As a reference, the chemical compositions of welded metals in the cases of curves 2 and 5 are shown in Table 9.

Table 9

	Chemical composition of welded metal (wt.%)										
	C	Si	Mn	P	S	Ni	Mo	Ti	B	Nb	V
Curve 2 Flux B & wire A	0.07	0.34	1.50	0.013	0.018	0.66	0.25	0.02	0.003	0.02	0.03
Curve 3 Flux B & wire I	0.07	0.33	1.25	0.013	0.030	0.73	0.26	0.02	0.001	0.02	0.02

Photographs (a) and (b) in FIG. 4 are the microstructure of welded metal showing the effect of this invention; (a) corresponds to the inventive example in curve 2 of FIG. 3(a), and (b) belongs to the comparison example in curve 5.

In (a), proeutectoid ferrites have almost disappeared and almost no acicular ferrites are observed. The sample consists of fine ferrite crystals, and shows high toughness. In (b), the proeutectoid ferrite grains are large, and its toughness is low.

As for the shape of filled-up wire used in the above experiments, a band-like metal tape was folded in a

As for the cored materials, a slag-forming agent, an arc stabilizer, a deoxidizer, alloy elements and iron, all being within the scope of this invention, can naturally be added besides metal fluorides (CaF_2 , MgF_2 , NaF , etc.), Ti and B.

As for the submerged arc flux, fused type ones were used in the above examples. Burnt or sintered type ones may also be applicable in this invention.

As above explained, according to this invention, the welding workability in one layer on both sides— and a small layer heap welding for low-temperature high tension steel, such as, low-temperature aluminum killed steel is excellent, and welded metal with high toughness can be obtained. Its economical effect is very great.

EXAMPLE 3

Aluminum killed steels containing Nb and V with the compositions shown in Table 10 were submerged arc welded in layer on both sides. The experimental results on the impact value of welded metals will be explained below.

The size of the master sheet was 11.7 mm in thickness, 200 mm in width and 400 mm in length. Notches as in FIG. 2 were made by a mechanical working, and the submerged arc welding was carried out under the conditions in Table 11. Impact test pieces were taken at the position shown in FIG. 1.

The welding was carried out under various combinations of six kinds of flux shown in Table 12 with 7 kinds of filled-up wire shown in Table 13. The combinations of submerged arc flux A, B and C with filled-up wires A, B and C are inventive examples (experiments Nos. 1-5).

Table 10

C	Si	Mn	Chemical composition of the steel sheet				Fe and impurities
			P	S	Nb	Al	
0.12	0.24	1.27	0.004	0.010	0.03	0.03	the remainder

complicated fashion. However, simple cylindrical and other shapes are, of course, effective for this invention.

While the rate of filling materials in the flux cored wire (filling ratio, in weight %), including iron powder, and others in total, was 18-26% in the above examples, it was ascertained that the manufacture of the wire is possible by using the rate of about 5-50% in general.

Table 11

Welding condition			
Back side	430 Amp.	30-35 volt	45 cm/min
Upper side	600 Amp.	32-38 volt	45 cm/min

Table 12

Flux	Chemical components in submerged arc flux (wt.%)								Basicity B
	SiO_2	CaO	MnO	MgO	TiO_2	Al_2O_3	CaF_2	Others	
A*	30	30	—	20	—	10	5	5	1.57
B*	34	7	17	8	5	2	25	2	1.29
C*	32	22	10	13	4	7	7	5	1.25
D	38	22	10	7	4	8	10	1	1.00
E	35	25	8	8	—	13	6	5	1.04
F	50	30	—	7	—	4	5	4	0.81

*flux necessary for this invention

13

Table 13

	Chemical components in submerged arc wire (wt.%) (projected, as filled-up wire)								
	Si	Mn	Ni	Mo	Ti	Al	Zr	B	
A*	0.2	2.0	1.5	0.5	0.2	—	—	0.020	5
B*	0.2	2.0	1.5	—	0.2	—	—	0.020	
C*	0.2	2.0	—	0.5	0.2	—	—	0.020	
D	0.2	2.0	1.5	0.5	—	0.3	—	0.020	
E	0.2	2.0	1.5	0.5	—	—	—	0.020	
F	0.2	2.0	1.5	0.5	—	0	0.3	0.020	
G	0.2	2.0	1.5	0.5	0.2	—	—	0.020	10

*wire necessary for this invention

Remarks: Said wires contained iron powder and a slag-forming agent besides above-mentioned components in order to control the rate of the filling material to the

14

Table 14-continued

Experiment No.	Experimental result		2 mm V notch, Charpy value, kg-m (mean value of 3 tests)	
	Flux	Wire	-60°C	-30°C
4*	B	A	6.9	14.6
5*	C	C	5.8	10.3
6	A	D	3.5	6.8
7	A	E	1.5	4.2
8	A	F	2.0	4.5
9	A	G	4.6	8.2
10	C	E	1.4	-6.0
11	D	A	2.1	6.7
12	E	A	2.5	7.0
13	E	C	1.0	4.3

*combination of this invention

Table 15

Experiment No.	Chemical components in the welded metal (wt.%)										
	C	Si	Mn	P	S	Ni	Mo	Ti	B	Nb	V
1	0.07	0.32	1.35	0.015	0.012	0.06	0.23	0.03	0.002	0.02	0.02
Flux A wire A											
7	0.07	0.30	1.38	0.013	0.014	0.52	0.23	<0.01	0.002	0.02	0.02
Flux A wire E											

total weight of the wire and to stabilize the arc. Si, Ti, Zr, B and other addition elements were used as an iron alloy powder or as a metal powder to obtain a definite composition.

A part of the experimental results on the impact test of the welded metal is shown in Table 14. Combinations Nos. 1, 4, 11 and 12 show the influence of flux basicity, showing that, even when the wire satisfies the condition of this invention, no substantial effect can be obtained when the submerged arc flux does not satisfy the conditions of this invention.

Nos. 1, 2, 3, 6, 7, 8 and 9 show that, even when the flux basicity satisfies the conditions of this invention, a welded metal with high toughness cannot be obtained when the composition of the wire does not satisfy the conditions of this invention.

Combinations Nos. 1, 2 and 3 show also that, only when the conditions of this invention are satisfied, a welded metal with high toughness can be obtained even if the alloy element varies over a wide range, for instance, no Ni or Mo is added.

As a reference, the chemical components in the welded metal in experiments Nos. 1 and 7 are shown in Table 6.

Table 14

Experiment No.	Experimental result		2 mm V notch, Charpy value, kg-m (mean value of 3 tests)	
	Flux	Wire	-60°C	-30°C
1*	A	A	2.3	12.4
2*	A	B	6.9	11.6
3*	A	C	7.1	13.2

EXAMPLE 4

A steel containing no Nb-V, N-Tuff 33 steel (normalized aluminum killed steel), and an Nb-V steel, a steel having nearly the same components as N-Tuff 33 steel, and also Nb-V, were selected as a steel sheet for the experiment.

The thickness of the sheet was 12 mm for N-Tuff 33 steel, and 11.7 mm for Nb-V steel. The chemical components therein were as shown in Table 16. The welding wires used were as shown in Table 17.

Three submerged arc fluxes, relatively acidic flux A, neutral flux B and highly basic flux C, were used. Their chemical components were as shown in Table 18. They were all of the fused type, and the grain size of the flux was under 20 mesh and contained dust.

The notch was a symmetrical X type with the root surface of 4 mm, and the notch angle was 90° on both sides.

As the welding condition, the backing pass was 500 A, 30-35 V, 45 cm/min. and the finishing pass was 600 A, 32-36, 45 cm/min.

The absorption energy values at -60°C in the 2 mm V notch Charpy test (side notch, whose position was at the center of welded metal and at the center of sheet thickness) of the welded metal obtained by welding with the above-mentioned conditions are shown in FIG. 5.

In Table 19, analytical values of the chemical components in the welded metal and in the slag on the surface of bead (finishing pass side in using wire A for Nb-V steel sheet) are given.

Table 16

	Chemical components in the steel sheet applied % chemical components %						
	C	Si	Mn	P	S	Nb	V
N-Tuff 33	0.10	0.26	1.20	0.017	0.006	—	—
Nb-V	0.12	0.24	1.27	0.014	0.010	0.03	0.03

Table 17

	Chemical components in the wire applied % chemical components %								
	C	Si	Mn	P	S	Ni	Mo	Ti	B
Wire A	0.06	0.10	1.32	0.011	0.009	1.20	0.42	0.10	0.008
Wire B	0.06	0.12	1.40	0.013	0.010	1.20	0.43	—	—

Table 18

Flux	Chemical components in the submerged arc flux applied Wt.%								
	SiO ₂	CaO	MnO	MgO	TiO ₂	Al ₂ O ₃	CaF ₂	Others	Basicity B
A	50	30	—	7	—	4	5	4	0.81
B	38	22	10	7	4	8	10	1	1.00
C	30	30	—	20	—	10	5	5	1.57

Table 19

	Chemical components in the welded metal and in the slag %						
	CaF ₂	Si	Mn	Ti	B	Nb	V
TA	15	0.2	1.8	0.3	0.015	0.06	0.06
TB	15	0.2	1.8	0.3	0.015	—	—

As it is obvious from these results, when a wire containing no Ti and B (wire B) is used in combination with any flux, the absorption energy value for Nb-V steel is equal to, or lower than the value for N-Tuf 33 steel.

On the contrary, when a wire containing Ti and B (wire A) is used, the Nb-V steel shows very high absorption energy value in the range where the slag basicity is high. Thus, it is obvious that by using the materials in this invention, a high toughness can be obtained in the case of the Nb-V steel.

EXAMPLE 5

Another experimental example showing that by using the materials of this invention the impact toughness of the welded metal is improved in the presence of Nb-V is set forth hereinbelow.

The steel sheet used was N-Tuf 33 steel (12 mm in thickness) as in Example 4, and the shape of notch and the welding conditions were also as in Example 4.

As a submerged arc flux, flux B in Example 4 was used.

Two kinds of flux cored wire (3.2 mm in diameter) as shown in Table 20 were used. Wire TA contains CaF₂-Si-Mn-Ti-B, and wire TB contains Nb-V in addition to these components.

The impact absorption energy values in 2 mm V notch Charpy test (side notch, whose position was at the center of welded metal and at the center of sheet thickness) of the welded metal by using the two wires are shown in Table 21 together with the chemical components in the slag and the welded metal.

As obvious from these results, the impact toughness is improved by the presence of Nb-V.

While the above experiments were compared for the steel of the Si-Mn system, a similar tendency was obtained when additional elements, such as, Ni, Cr and Mo, were also added. Therefore, it is clear that this invention can be applied to a 60-80 kg/mm² class high tension steel.

It is also clear that this invention can be applied only when the contents of Ti, B and Nb (V) lie within the scope of this invention, for a welded metal of the 50-80 kg/mm² class steel containing other elements, such as, C, Si, Mn, Cu, P, Ni, Cr and Mo.

Trace elements, such as, Al and Zr have no effect on this invention.

As explained above in detail, by using the welding materials of this invention, a welded metal with high toughness can be obtained in the welding of Nb-V steel which gives usually a welded metal with low impact values. Its economical merit is very great.

Table 20

Wire	Absorption energy		Chemical components in the welded metal (%)							Chemical components in the slag (%)						
	-60°	-30°	O	Si	Mn	Ti	B	Nb	V	SiO ₂	CaO	MnO	MgO	TiO ₂	Al ₂ O ₃	
TA	8.3	12.2	0.07	0.30	1.45	0.04	0.004	0.03	0.02	31.9	16.9	17.3	3.1	3.4	0.9	
TB	3.3	8.3	0.07	0.31	1.46	0.03	0.003	—	—	—	—	—	—	—	—	
Wire	CaF ₂	FeO	Basicity b													
TA	18.9	2.2	1.43													
TB	—	—	—													

Table 21

No.	Steel Sheath	Flux	Wire	Additive	Chemical components in the welded metal										
					C	Si	Mn	P	S	Ni	Mo	Ti	S	Nb	V
1			A	—	0.07	0.40	1.21	0.013	0.013	0.41	0.10	0.01	0.002	0.03	0.02
2			B	—	0.07	0.38	1.26	0.014	0.012	0.45	0.19	—	—	0.03	0.02
3			A	—	0.08	0.30	1.26	0.014	0.014	0.44	0.19	0.02	0.002	0.03	0.03
4			B	—	0.08	0.30	1.26	0.014	0.012	0.45	0.19	—	—	0.02	0.02
5			A	CaF ₂ added	0.07	0.22	1.31	0.013	0.009	0.43	0.21	0.02	0.002	0.03	0.02
6	Steel		B	"	0.08	0.24	1.32	0.013	0.010	0.42	0.22	—	—	0.03	0.02

Table 21 -continued

No.	Steel Sheath	Flux	Wire	Additive	Chemical components in the welded metal											
					C	Si	Mn	P	S	Ni	Mo	Ti	S	Nb	V	
7	N-Tuf	C	A	—	0.10	0.22	1.25	0.013	0.008	0.42	0.19	0.01	0.002	0.03	0.03	
8			B	—	0.10	0.020	1.27	0.012	0.008	0.45	0.20	—	—	0.03	0.03	
9		A	—	0.08	0.38	1.20	0.015	0.013	0.42	0.17	0.02	0.001	—	—		
10		A	B	—	0.08	0.38	1.24	0.015	0.013	0.43	0.19	—	—	—	—	
11			A	—	0.07	0.32	1.28	0.015	0.012	0.43	0.21	0.02	0.002	—	—	
12		A	B	—	0.09	0.31	1.30	0.015	0.012	0.46	0.20	—	—	—	—	
13			A	CaF ₂ added	0.09	0.27	1.30	0.014	0.010	0.39	0.17	0.02	0.002	—	—	
14		33 Steel	C	B	—	0.08	0.28	1.35	0.015	0.011	0.41	0.18	—	—	—	—
15				A	—	0.10	0.25	1.27	0.015	0.009	0.48	0.20	0.01	0.002	—	—
16				B	—	0.10	0.25	1.29	0.013	0.008	0.47	0.21	—	—	—	—

Chemical components in the welded metal basicity b and slag														
No.	Steel Sheath	Flux	Wire	Additive	SiO ₂	CaO	MnO	MgO	TiO ₂	Al ₂ O ₃	CaF ₂	FeO		
1	Nb-V	A	A	—	49.5	27.1	0.6	0.9	—	4.0	4.8	4.8	0.85	
2			B	—										
3		B	A	—	38.3	17.5	20.5	4.0	3.8	2.1	8.5	4.0	1.02	
4			B	—										
5		B	A	CaF ₂	32.1	17.0	18.2	3.0	3.1	1.4	1.5	2.5	1.32	
6	B		added											
7	Steel	C	A	—	28.4	28.3	0.4	19.1	—	9.0	4.5	1.3	1.60	
8			B	—										

What is claimed is:

1. In a method of submerged arc welding to obtain a welded metal with high toughness, the improvement which comprises using in combination:

- a. a submerged arc flux having a nearly neutral composition and having a basicity b as expressed by formula (1) herein in the range from about 0.90 to 1.30, wherein

$$b = \frac{\text{CaO} + \text{MgO} + \text{BaO} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Li}_2\text{O} + \text{CaF}_2 + \frac{1}{2}(\text{MgO} + \text{FeO})}{\text{SiO}_2 + \frac{1}{2}(\text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{ZrO}_2)}$$

the amounts of the compounds being expressed in weight per cent based on the weight of the flux; and

- b. a wire composed of a hollow-core mild steel sheath, said core being packed with a powdered mixture of about 0.04 to 1.0% by weight titanium,

about 0.002 to 0.05% by weight boron, and about 4 to 25% by weight of a fluoride compound selected from the group consisting of CaF₂, NaF₂, KF, LiF, MgF₂, MnF₂, and combinations thereof, all weights being based on the weight of the wire and the balance of the weight of the wire being the steel sheath.

2. The method of claim 1 wherein the welded metal

contains up to 3.5% by weight Ni.

3. The method of claim 1 wherein the welded metal contains up to 0.8% by weight Mo.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3924091

Dated December 2, 1975

Inventor(s) Haruyoshi Suzuki et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading of the Letters patent [75] and [30] should read as follows:

--[75] Haruyoshi Suzuki, Tokyo;
Tsuyoshi Takino, Chiba-ken;
Naomichi Mori, Tokyo;
Isao Sugioka, Chiba-ken;
Osamu Matsuda, Chiba-ken;
Shozo Sekino, Fukuoka-ken;
Hiroyuki Honma, Tochigi-ken,
all of Japan--.

--[30] Aug. 12, 1970 Japan.....45-71058
Sept. 29, 1970 Japan.....45-84613
Aug. 14, 1970 Japan.....45-71575
Dec. 10, 1970 Japan.....45-109847--.

Signed and Sealed this

sixteenth Day of March 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

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Signed and Sealed this
sixteenth Day of March 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

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Commissioner of Patents and Trademarks

JP58135793 A
FLUX CORED(^) WIRE FOR SUBMERGED ARC(^) WELDING
NIPPON OIL & FATS CO LTD

Abstract:

PURPOSE: To perform welding with easy start of arc(^) and high stability of arcs at a high rate of deposition by using a flux cored(^) wire of a specific compsn. contg. stainless steel powder in submerged arc(^) welding of stainless steel.

CONSTITUTION: A flux of the following compsn. is packed in a stainless steel hollow wire of the same material as the stainless steel to be welded as a flux cored(^) wire to be used in submerged arc(^) welding of stainless steel: A flux which contains 0.5W20% 1 or ≥ 2 kinds among rutile, ilmenite and zircon sand by weight of the wire, 0.05W3% 1 or ≥ 2 kinds among potash feldspar, silica and wollastonite, 0.2W5% 1 or ≥ 2 kinds among calcium carbonate, lithium carbonate and barium carbonate, 0.3W2% fluorides such as CaF_2 and wherein stainless steel powder is so mixed at $\leq 25\%$ ratio that weld metal and the materials to be welded have the same compsn.

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JAPIO Class: 12.5 (METALS -- Working)

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ABSTRACT

PURPOSE: To perform welding with easy start of arc and high stability of arcs at a high rate of deposition by using a flux cored wire of a specific composition containing stainless steel powder in submerged arc welding of stainless steel.

CONSTITUTION: A flux of the following composition is packed in a stainless steel hollow wire of the same material as the stainless steel to be welded as a flux cored wire to be used in submerged arc welding of stainless steel: A flux which contains 0.5-20% 1 or ≥ 2 kinds among rutile, ilmenite and zircon sand by weight of the wire, 0.05-3% 1 or ≥ 2 kinds among potash feldspar, silica and wollastonite, 0.2-5% 1 or ≥ 2 kinds among calcium carbonate, lithium carbonate and barium carbonate, 0.3-2% fluorides such as CaF_2 and wherein stainless steel powder is so mixed at $\leq 25\%$ ratio that weld metal and the materials to be welded have the same composition

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⑮ サブマージアーク溶接用フラックス入りワイヤ

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明 細 書

1. 発明の名称

サブマージアーク溶接用フラックス入りワイヤ

2. 特許請求の範囲

ステンレス鋼の管状ワイヤの内部空間に、ワイヤ重量比で、ルチル、イルミナイトまたはジルコンサンドの1種または2種以上を0.5～20%、カリ長石、シリカまたは珪灰石の1種または2種以上を0.05～3%、炭酸カルシウム、炭酸リチウムまたは炭酸バリウムの1種または2種以上を0.2～5%、弗化物を0.3～2%およびステンレス鋼粉末を主体とする金属粉末を25%以下充填してなるサブマージアーク溶接用フラックス入りワイヤ。

3. 発明の詳細な説明

本発明は、ステンレス鋼のサブマージアーク溶接に使用するフラックス入りワイヤに関する。

従来、粒状のフラックスとソリッドワイヤを組

合せて行うステンレス鋼のサブマージアーク溶接は、溶接温度が早くて効率が良いため、被覆アーク溶接やフラックス入りワイヤによるミグ溶接に代つて一般に行われている。

しかしながら、被覆アーク溶接やフラックス入りワイヤによるミグ溶接に比べ、溶込みが深く、アークの安定性が悪く、また下向きだけでしか溶接できない等の欠点がある。さらに目的の溶着金属化学成分を得るためには、それに近い化学成分のソリッドワイヤを用いる必要があり、それがためそれぞれの目的用途に応じて、成分を調整したソリッドワイヤを特別に製造する必要がある。

本発明は、かかるステンレス鋼のサブマージアーク溶接に、ソリッドワイヤを用いることに基づく欠点をワイヤ重量比でルチル、イルミナイトまたはジルコンサンドの1種または2種以上を0.5～20%、カリ長石、シリカまたは珪灰石の1種または2種以上を0.05～3%、炭酸カルシウム、炭酸リチウムまたは炭酸バリウムの1種または2種以上を0.2～5%、弗化物を0.3～2%および

目的成分に合せたステンレス鋼粉末を主体とする金属粉末を25%以下含有するフラックス入りワイヤを用いることにより解決するものである。

すなわち、本発明では、ワイヤにフラックスが入っているため、ソリッドワイヤに比べて同一電流・電圧での溶着速度が大きく、浅溶込みで母材への熱影響が軽減され、フラックス中のアーク安定剤、ガス発生剤の存在によりアークスタートが容易で、かつアークの安定性が良く、スラグ形成剤の存在により横向き溶着でもビードの垂れがなく、形状が良好でスラグの剝離性良く、特殊な溶着金属化学成分もフラックス中の金属粉末の配合調整で容易に得ることが可能である。

本発明ワイヤの構成物質ならびに量による効果を説明する。

本発明のワイヤの外皮にステンレス鋼を使用することは、本発明の特徴の一つである。ここでステンレス鋼とは、12~40%のCrおよび0~40%のNiを含有するFe-CrあるいはFe-Cr-Niを主要成分とする合金鋼のことである。

いるが、配合量がワイヤ重量比で0.5%未満では凝固後のスラグの溶着金属との分離性が悪くなり、20%を越えるとスラグの粘稠度が大き過ぎて溶着性を低下させるため0.5~20%とする。

(ii) カリ長石、シリカおよび珪灰石はアークの安定性を増し、溶着金属とスラグに流動性を与えるとともに溶着金属と母材のなじみ性を向上し、ビードの外観、形状を良好にする。配合量がワイヤ重量比で0.05%未満では作用が不十分で効率が不足し、3%を越えると凝固スラグが固すぎて剝離性を損うため0.05~3%とする。

(iii) 炭酸^{カルシウム}カルシウム、炭酸リチウムおよび炭酸バリウムは溶着時のアーク熱によつて熱分解し、炭酸ガスを発生して溶着金属を大気から遮断するとともにアークを安定にし、スラグを軟質化して剝離性を良好にする。配合量がワイヤ重量比で0.2%未満ではその作用が不十分であり、5%を越えるとガスの発生が多くて溶着作業の障害となるため、0.2~5%とする。

(iv) 弗化物はワイヤの先端からの溶滴生成、移

る。

ステンレス鋼の溶着金属を得るためには、外皮に鉄あるいはこれに近い成分の材料を使用し、内包フラックスからCr、Niなどの合金元素を添加することもできるが、これでは溶着金属の化学成分、組織の均一性が損われ、特に冷却速度が早い場合、すなわち溶着金属の凝固が速い場合に、フラックスと外皮が十分均一に溶融混合せず、好ましい溶着金属が得られない。またワイヤは溶着時アーク端に至る間に通電によつて抵抗発熱し、ワイヤ端における溶滴の生成および溶融速度の増大を導くものであるため、以上の理由から電気抵抗が大きいステンレス鋼の外皮が必要とされるのである。

次に本発明のワイヤに充填されたフラックスについて説明する。

(i) ルチル、イルミナイトおよびジルコンサンドはスラグ形成剤であつて、溶着時に適当な粘稠性を有し、かつ凝固後は脆弱で溶着金属との分離が容易である。単体または2種以上を組合せて用

行を促進し、アークを安定させ、また溶融スラグの流動性を増加させる。弗化物としては CaF_2 、 NaF 、 BaF_2 、 MgF_2 、 AlF_3 、 Na_3AlF_6 、 K_2SiF_6 、 Na_2SiF_6 、 K_2TiF_6 などであつて、単体あるいは混合物の形で使用される。配合量がワイヤ重量比で0.3%未満では溶着の生成、移行が十分でなく、2%を越えるとアークの安定性を害するので、0.3%~2%とする。

(ii) 金属粉末はFe、Cr、Ni、Mn、Mo、Cu、Nb、Co、V、W、Al、Ti、Mg、Zr、Siなどの単独あるいは合金粉末の形で、溶着金属の要求に応じて金属外皮の化学成分との組合で配合量がワイヤの重量比で25%以下で適当に配合される。

以下実施例、比較例により本発明を具体的に説明する。

(1) フラックス入りワイヤの製造

JIS 304Lのステンレス鋼フープをワイヤ外皮とし、表1表に配合を示すフラックスを用いて、冷間ロール成形方式により直径が3.2mmの夾

実施例1～8のフラックス入りワイヤを製造した。

第1表 ワイヤの構成(単位重量%)

		実 施 例							
		1	2	3	4	5	6	7	8
フ ラ ク ス 成 分	CaF ₂	1	1	0.3		1	0.5	1	0.5
	Na ₂ P		0.5		2			0.5	0.3
	CaCO ₃	4	1	2	0.2	0.5	0.5	2	0.5
	Li ₂ CO ₃	1	2			0.5		1	
	BaCO ₃		1						0.5
	カリ長石	2	1	1	0.05	2	1	2	1.5
	シリカ		0.5						0.5
	珪灰石		1			1		1	
	スルチル	12	15	15	7		2	0.5	4
	イルミナイト	2		1		2			1
	ジルコンサンド			4		10	3		2
	Cr	5	4	4	10	7	4	3	6
	Ni	1	1	1	3	3	0.5	1	1
	Mn	2	2	1	2	2	0.5	1	1
	8U8304			0.7	8.05	1	3	2	6.2
フラックス合計		30	30	30	30	30	15	15	25
ワイヤ外皮		70	70	70	70	70	85	85	75

(B) 溶接試験

実施例1～8のフラックス入りワイヤと焼結型フラックスを用いて、材質が8U8304で開先巾30mm、開先深さ2.6mm、開先角度60度の開先を持つ、高さ80mm、奥行き80mmの母材のV型開先内に、第2表の溶接条件で下向きおよび横向き溶接を行った。

同様条件で、8U8308ソリッドワイヤと焼結型フラックスを用いて比較例の下向きおよび横向き溶接を行った。

第2表 溶接条件

溶接姿勢	下向き	横向き
電 流 (A)	400	300
電 圧 (V)	30	30
溶接速度 (mm/min)	300	400

溶接試験結果を第3表に示す。

第3表から明らかなように、実施例1～8はアークスタートおよびアークの安定性が良好で、ビード形状は下向きで山崎でなく、横向きで垂れが

第3表 溶接試験結果

	溶接 姿勢	アークの スタート	アークの 安定性	ビードの 形状	スラグの 剝離性	溶 着 速 度 (mm/min)	母材溶 込み率(%)
実施例1	下向	良好	良好	偏平	自然剝離	145	16
	横向	良好	やや悪い	偏平	自然剝離	98	13
2	下向	良好	良好	偏平	自然剝離	132	15
	横向	良好	良好	偏平	自然剝離	100	12
3	下向	良好	やや悪い	やや山高	自然剝離	128	17
	横向	良好	やや悪い	やや山高	自然剝離	88	13
4	下向	良好	やや悪い	偏平	自然剝離	142	14
	横向	良好	良好	ややたれる	取れ易い	105	11
5	下向	良好	良好	偏平	やや取れにくい	136	16
	横向	良好	良好	偏平	やや取れにくい	92	10
6	下向	良好	良好	偏平	やや取れにくい	113	20
	横向	良好	やや悪い	ややたれる	取れ易い	75	15
7	下向	良好	良好	やや山高	やや取れにくい	110	19
	横向	良好	良好	ややたれる	やや取れにくい	69	14
8	下向	良好	良好	偏平	自然剝離	125	18
	横向	良好	良好	偏平	自然剝離	88	12
比較例	下向	不良	やや悪い	山高	取れにくい	93	26
	横向	不良	悪い	たれる	取れにくい	63	18

無く、冷却後スラグは取れ易くて自然剝離し、~~溶~~融速度が大きく、溶込みが浅い。

これに対し、比較例はアークスタートおよびアーク安定性が悪く、ビード形状は下向き姿勢では山高で、横向き姿勢では垂れ、冷却後のスラグが剝離しにくく、~~溶~~融速度が小さく、深溶込みである。

以上のごとく、本発明のサブマージ^(ア-2)溶接用フラックス入りワイヤは、サブマージ^(ア-2)溶接に用いて、従来のソリッドワイヤを用いた場合に比べ優れた特徴を有するものである。

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Table 1 - Wire Construction (Unit = Weight %)

	Embodiments							
	1	2	3	4	5	6	7	8
CaF ₂	1	1	0.3		1	0.5	1	0.5
Na F		0.5		2			0.5	0.3
CaCo ₃	4	1	2	0.2	0.5	0.5	2	0.5
Li ₂ CO ₃	1	2			0.5		1	
BaCO ₃		1						0.5
Potash feldspar	2	1	1	0.05	2	1	2	1.5
Silica		0.5						0.5
Wollastonite		1			1		1	
Rutile	12	15	15	7		2	0.5	4
Ilmenite	2		1		2			1
Zirconium Sand			4		10	3		2
Cr	5	4	4	10	7	4	3	6
Ni	1	1	1	3	3	0.5	1	1
Mn	2	2	1	2	2	0.5	1	1
SUS304			0.7	80.5	1	3	2	6.2
Flux total	30	30	30	30	30	15	15	25
Wire Sheath	70	70	70	70	70	85	85	75

JP63212092 A
**SEAMLESS FLUX CORED(^) WIRE FOR SUBMERGED ARC(^) FILLET
WELDING**
NIPPON STEEL CORP

Abstract:

PURPOSE: To obtain a seamless flux cored(^) wire for submerged arc(^) fillet welding having excellent pit resistance by incorporating chloride and fluoride into the wire at specific ratios with respect to the total weight of the wire.

CONSTITUTION: This seamless flux cored(^) wire for submerged arc(^) fillet welding contains the chloride at 0.02W0.20% in terms of C with respect to the total weight of the wire and the fluoride at 0.10W2.00% in terms of F. If the chloride and fluoride are made to co-exist in the wire in such a manner, the hydrogen generated from red rust and primer is extremely smoothly captured in the form of hydrogen fluoride in an arc(^) atmosphere by utilizing the interaction of the chlorine and fluorine formed by the cracking reaction thereof, by which the amt. of the hydrogen to be dissolved into a molten metal is decreased.

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ABSTRACT

PURPOSE: To obtain a seamless flux cored wire for submerged arc fillet welding having excellent pit resistance by incorporating chloride and fluoride into the wire at specific ratios with respect to the total weight of the wire.

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⑨ 日本国特許庁(JP)

⑩ 特許出願公開

⑪ 公開特許公報(A)

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⑭ 発明の名称 すみ肉溶接用シームレスフラックス充填ワイヤ

⑮ 特 願 昭62-44025

⑯ 出 願 昭62(1987)2月26日

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明 細 書

1. 発明の名称

すみ肉溶接用シームレスフラックス充填ワイヤ

2. 特許請求の範囲

(1) ワイヤ超重量に対し、亜酸化セシ換算量で0.02~0.20%、および亜硫酸セシ換算量で0.10~2.00%含有することを特徴とするすみ肉溶接用シームレスフラックス充填ワイヤ。

3. 発明の詳細な説明

(産業上の利用分野)

本発明はすみ肉溶接用シームレスフラックス充填ワイヤに関し、特に腐食の発生した鋼板、あるいは防錆プライマを塗布した鋼板などのすみ肉溶接部に使用するワイヤに優れたすみ肉溶接用シームレスフラックス充填ワイヤに関する。

(従来の技術)

鉄骨、橋梁等のすみ肉溶接部において現場施工上最も重要な腐蝕点は、鋼板表面に発生した腐

び、あるいは防錆のために塗布されたプライマに起因するピットの発生である。このピットの発生原因は、すみ肉電極の上部(ウェット)と下部(フランク)との液なり部およびその近傍(溶接部)に存在する赤錆やプライマが溶接熱によって分解あるいは燃焼してガス化し、このガスの一部が溶融金属中に多量に溶解し、さらに比較的小入熱溶接条件で行なわれるすみ肉溶接においては溶融金属の凝固速度が大きく、溶解したガスは凝固過程で外部へ放出されず、ガスの放出孔が閉じる前に凝固の溶融金属が凝固してしまうことによりビード表面に口を開いたものと考えられる。従って、ピットを発生しにくくするためには、溶融金属中へのガスの溶解量をできるだけ少なくすると同時に、溶融金属中に溶解したガスについても速やかに外部へ放出しやすくすることが必要となり、従来よりこの観点から溶接方法および溶接材料の両面より種々の提案がなされている。

例えば、特公明58-14399号公報は、水

平すみ肉溶氩溶接におけるビッド発生防止のために上板端面を開先加工し、ガス逃げ用空隙を設けて付なり溶接方法が効果的であることを開示している。本発明者らも上板と下板を仮組溶接する際には溶子の間隙を設けた場合、ビッドの発生がかなり抑制できることを確証しているが、鋼板の開先加工や1mm以下の空隙を設けて仮組溶接を行なうことは困難であり、製造コストおよび組立面から現場的な実用性に欠けるものである。

溶接材料面ではこれまでに溶接用フラックスについて検討され、フラックスの結水還元とともに成分としてCaF₂を含有させ、CaF₂→Ca+2F、H+F→HFの反応により溶きびやブライマから発生した水素を弗化水素として捕捉し、溶融金属中へのガスの溶解量を少なくすることが耐ビッド対策として有効であることが知られている。さらに特公昭57-20079号公報においては弗化亜鉛(CaF₂)を含有する溶接用フラックスを提案し、弗化亜鉛の作用としてアーク雰囲気中の水素分圧を下げる効果以外に、溶融金属の侵

蝕効果によりいったん溶融したガスの外部への放出が容易になることを開示している。しかし、ビッドの発生を防止しようとして溶接用フラックス中にCaF₂を多量に含有させた場合、スラグが流れやすくなるためビッド形状が不良となり、また弗化亜鉛を含有する溶接用フラックスについても溶きび発生やブライマ塗布鋼板のすみ肉溶氩溶接に使用した場合、耐ビッド性は十分でない。

従来、この種のすみ肉溶氩溶接用のワイヤについては、通常ソリッドワイヤが使用されているが、上記特公昭57-20079号公報の実施例中には弗化亜鉛を含有する半自動溶接用のフラックス充填ワイヤの記載がある。またガスシールドアーク溶接用のフラックス充填ワイヤに弗化物を含有させることは従来より一般的であり、これは耐ビッド性に対しては前記フラックス中に弗化物を含有させることと同様の効果をもつと考えられる。なお、最近の特開昭61-17995号公報は水ガラスを添加、造粒して充填するフラックスで問題となる溶接強度の改善のためにCl⁻イオンを含

有する溶接用フラックスを提案したものであるが、その実施例中に、多量の弗化物とともに極めて微量のCl⁻イオンを含有するフラックス充填ワイヤの記載がある。しかし、これらのフラックス充填ワイヤを溶きびの発生した鋼板やブライマ塗布鋼板のすみ肉溶氩溶接に使用した場合、いずれもソリッドワイヤを使用した場合と同様に耐ビッド性が十分でなく、ビッド形状も低くなるなどの問題がある。

このため、溶きびの発生した鋼板や防錆ブライマ塗布鋼板のすみ肉溶氩溶接は、最近の工設低減、高率向上の要求にもかかわらず溶きびやブライマをグライNDERなどで除去してから溶接が行なわれている。

(発明が解決しようとする問題点)

そこで、本発明は溶きびや防錆ブライマを除去しないですみ肉溶氩溶接を行なった場合でもビッド欠陥が発生しにくいすみ肉溶氩溶接用材料の提供を目的とする。

(問題点を解決するための手段)

本発明の要旨は、ワイヤ線重量に対し、弗化物をCl⁻換算量で0.02~0.20%、および弗化物をF換算量で0.10~2.00%含有することを特徴とするすみ肉溶氩溶接用シームレスフラックス充填ワイヤにある。

(作用)

本発明者らは、溶きびあるいは防錆ブライマ塗布鋼板のすみ肉溶氩溶接において問題となるビッドの発生を防止するために溶接材料面から種々検討した結果、極めて微量の弗化物和弗化物とを共存させてそれぞれ微量の範囲で含有するシームレスフラックス充填ワイヤにより所期の目的を達したものである。

まず、本発明のシームレスフラックス充填ワイヤに弗化物和弗化物とを共存させて含有させることは、溶接時のこれらの分解反応により生成する塩素と弗素の相互作用を利用し、溶きびやブライマから発生する水素をアーク雰囲気中で極めてスムーズに弗化水素として捕捉し、溶融金属中への水素の溶解量を少なくするためである。

例えば塩化物として NaCl 、弗化物として CaF_2 を含有させた場合、 $\text{NaCl} \rightarrow \text{Na} + \text{Cl}$ 、 $\text{CaF}_2 \rightarrow \text{Ca} + 2\text{F}$ の分解反応によりアーク雰囲気中には塩素および弗素が生成し、これらと水素は次のような反応を起こす。アーク底下では塩素と水素との反応が先行し塩化水素を生成し、この塩化水素は弗素と速やかに反応する性質をもつため以下の反応により容易に弗化水素となり得る。 $\text{H} + \text{Cl} \rightarrow \text{HCl}$ 、 $\text{HCl} + \text{F} \rightarrow \text{HF} + \text{Cl}$ 。つまり、塩化物と弗化物とをワイヤ中に共存させる効果は、弗化物のみをワイヤ中に含有させた場合に比べ極めてスムーズに水素を弗化水素として捕捉することが可能となる。また、すみ肉溶接に使用される俗称用フラックスは通常 CaF_2 を少量含有しているが、その分解温度が高く水素と反応して弗化水素となる弗素の供給が不十分であるのに対し、ワイヤ中に含有させることによりアークの高温下で $\text{CaF}_2 \rightarrow \text{Ca} + 2\text{F}$ の分解が促進される。

次に、塩化物および弗化物の含有量については試作ワイヤにより詳細に検討を行なった結果、塩

化物はワイヤ総重量に対し、 Cl 換算量（塩化物中の Cl 量、例えば NaCl の場合、 NaCl 重量 $\times 0.50$ ）で 0.02 重量% 以上は上記弗化物との共存効果はあまり認められず、ビード欠陥の発生防止のためには 0.02 重量% 以上含有させる必要がある。しかし、塩化物は作業環境上でもるだけ微量であることが好ましいこと、また塩化物を多量に含有させた場合、ビードの均一性が不良となる傾向を示すことや、前記 $\text{H} + \text{Cl} \rightarrow \text{HCl}$ の反応で発生した塩化水素の一部はアーク雰囲気中で炭素ガスと反応し塩化鉄を生成するようであり、溶接後の放電によりビード表面に赤かっ色のきび状のものが付着することなどから、上限を 0.10 重量% に限定した。弗化物は、俗称用フラックス中に通常含有される成分（特に CaF_2 ）であるが、ワイヤ中に含有させることによってさらに上記塩化物との共存効果を発揮させることができる。このために弗化物はワイヤ総重量に対し、 F 換算量（弗化物中の F 量、例えば CaF_2 の場合、 CaF_2 重量 $\times 0.40$ ）で 0.10 重量% 以上含有させる必要がある。しかし、弗化物の含有量

が多すぎて F 換算量で 3.00 重量% を超えるとアーク不安定、ビード形状不良、ビード外観不良（スパッタ付着）、スラグ剥離性不良など溶接作業性への悪影響が目立つようになる。

なお、上記塩化物および弗化物の種類については特に限定するものでないが、塩化物としては NaCl 以外に KCl 、 CaCl_2 、 BaCl_2 、 MgCl_2 などとよく、弗化物としては CaF_2 以外に KF 、 NaF 、 LiF などとよい。

また、塩化物および弗化物以外の充満フラックス成分についても特に限定するものでなく、 SiO_2 、 MnO 、 CaO 、 MgO 、 Al_2O_3 、 TiO_2 、 ZrO_2 などのスラグ形成剤、 CaCO_3 、 MgCO_3 、 BaCO_3 などのガス発生剤、 Fe-Si 、 Fe-Mn 、 Al などの脱酸剤、 Ni 、 Mo などの合金剤、さらに Fe 粉などによい。ワイヤ総重量に占める充満フラックス部の割合は溶接作業性および溶着効率を考慮し 5～30 重量% であることが好ましい。

本発明においては、上記塩化物および弗化物は

レームレスフラックス入りワイヤに充満するものであるが、これは上記成分が潤滑性あるいは吸湿性を有する成分で、溶接用フラックス中に添加したのでは俗称用フラックスの吸湿性が著しく増加し溶接性を損なうことによるものである。さらにレームレスフラックス入りワイヤに充満したことにより以下の効果をもつ。前記のように塩化物と弗化物の共存効果は赤きびや粉状アライマから発生するガスを溶融金属中に溶解しにくくすることにあるが、いったん溶融金属中に溶解したガスを凝固過程で速やかに外部へ放出させるためにレームレスフラックス充満ワイヤは極めて有効である。即ち、レームレスフラックス充満ワイヤの特性として、ソリッドワイヤを使用した場合に比べ溶込みの浅いビード、つまり浅い溶融池を形成しながら溶接が進行すること、さらに塩化物および弗化物の一部が直接溶融池に吹きつけられ溶融金属の溶接が十分となることによりガスの放出が促進される。

以下、本発明の効果をさらに実施例により具体

的に示す。

(実施例)

第1表に示す成分の充填フラックス(CF1-CF11)を第2表に示す成分の銅管フープ(P1)に充填後、導引、焼鈍(850℃)、導引の工程を経て、第3表に示す成分のシームレスフラックス充填ワイヤ(FW1~13、ワイヤ径2.0mmφ)を試作製造した。なお、第4表には比較のために供試したソリッドワイヤ(SW1、ワイヤ径2.0mmφ)の成分を示す。これらワイヤと第5表に示す成分の溶接用フラックス(F1、F2)とを組合せて、ソングリッパプライマを約25μの厚さに塗布した板厚12.7mmのSM-50鋼を第1図(a)に示すように仮組溶接(上板と下板の間隙は0.1mm以下)し、AC電極、380V、57V-50.0mm/minの溶接条件で第1図(b)に示すように水平すみ肉溶接試験を行った。第6表に試験結果をまとめて示す。

試験No.1~8およびNo.15は本発明によるシームレスフラックス充填ワイヤ(FW1~8)

を使用した場合で、いずれもビットの発生がなく、またスラグ粘性、ビードの均一性とも良好であった。これに対し、No.9~14およびNo.16、17は比較ワイヤ(FW9~12、SW1)を使用した場合である。No.9およびNo.16はワイヤ(FW9)の酸化物の含有量が少なすぎるためにビットが発生し、逆にNo.10はワイヤ(FW10)の酸化物の含有量が多すぎるためにビードに乱れが生じた。No.11はワイヤ(FW11)に酸化物が含有されていないために、No.12はワイヤ(FW12)の酸化物の含有量が少なすぎるためにそれぞれビットが発生した。No.13はワイヤ(FW13)の酸化物の含有量が多すぎるためにスラグ粘性不良(スラグ付着)、ビードの均一性不良(波目粗く、形状不良)となった。No.14およびNo.17はソリッドワイヤ(SW1)を使用した場合でいずれもビットが発生した。

第1表 充填フラックスの成分(重量%)

充填フラックス記号	SiO ₂	MnO	CaO	MgO	Al ₂ O ₃	TiO ₂	CaCO ₃	Fe-Si	Fe粉	その他				
CF1	0.1	-	-	8.0	45.0	37.0	2.0	8.8	4.0	-	-	-	3.6	
CF2	0.3	-	-	8.0	44.9	39.9	2.0	8.0	4.0	-	-	-	8.0	
CF3	1.5	-	-	8.0	44.8	38.4	2.0	5.9	8.8	-	-	-	5.0	
CF4	4.0	-	-	2.9	43.2	35.5	1.8	5.8	9.8	-	-	-	2.9	
CF5	1.0	-	-	+	48.5	39.6	2.0	5.0	9.0	-	-	-	8.0	
CF6	0.8	-	1.0	+	48.8	39.3	2.0	4.9	2.9	-	-	-	1.8	
CF7	0.8	-	-	15.0	39.6	33.7	1.7	4.2	2.5	-	-	-	2.5	
CF8	0.5	0.5	-	3.0	45.0	24.0	6.0	10.0	4.0	3.0	-	-	4.0	
CF9	-	1.0	-	25.0	34.0	18.0	4.5	7.5	8.0	2.5	-	-	4.5	
CF10	1.0	-	0.5	3.0	10.0	14.0	2.0	3.0	41.0	15.0	-	2.0	4.5	
CF11	6.5	-	0.5	5.0	34.0	30.0	1.5	1.5	3.0	-	2.0	3.0	15.0	4.0

1) その他成分はK₂O、Na₂O、FeO、および不可避不純物など。

第2表 銅管フープの化学成分(重量%)

銅管フープ記号	C	Si	Mn	P	S
P1	0.13	0.61	1.50	0.005	0.001

[illegible]

1) その他成分は K_2O 、 Na_2O 、 FeO および不可溶不純物など。

中実ワイヤ記号	C	Si	Mn	P	S
SW1	0.12	0.02	1.90	0.012	0.007

溶接用フラックス記号	SiO ₂	MnO	CaO	MgO	Al ₂ O ₃	TiO ₂	CaF ₂	その他
F1	45	87	2	6	4	—	3	3
F2	12	14	2	3	41	15	7	8

1) フラックス記号 F1: 海産型珪石状フラックス
F2: 焼成型フラックス
2) その他成分は K_2O 、 Na_2O 、 FeO 、 $Fe-Si$ 、 $Fe-Mn$ 、および不可避不純物など。

試験 NO.	ワイヤ 配 号	接 着 用 フラスコ 番 号	ビッド発生数 (ビッド発生 当り(個))	ス ラ 料 質 性	ビ ド 均 一 の 性	判 定	
			1st 間	2nd 間			
1	FW1	F 1	0	0	良好	良好	合格
2	FW2		0	0	良好	良好	合格
3	FW3		0	0	良好	良好	合格
4	FW4		0	0	良好	良好	合格
5	FW5		0	0	良好	良好	合格
6	FW6		0	0	良好	良好	合格
7	FW7		0	0	良好	良好	合格
8	FW8		0	0	良好	良好	合格
9	FW9		4	12	良好	良好	不合格
10	FW10		0	0	良好	不良	不合格
11	FW11	F 2	1	5	良好	良好	不合格
12	FW12		2	4	良好	良好	不合格
13	FW13		0	0	不良	不良	不合格
14	SW1		3	15	良好	良好	不合格
15	FW3		0	0	良好	良好	合格
16	FW9		5	18	良好	良好	不合格
17	SW1		2	12	良好	良好	不合格

本発明は、表面に赤さびが発生した鋼板や防錆プライマ塗布鋼板のすみ肉部溶解液において副産物となっているピットの発生を極めて効果的に防止することも可能にしたすみ肉部溶解液用シーメンスフラックス充満ワイヤであり、工業的実用性は高い。

第1図(a)は水平すみ肉溶接試験における仮組状況、同図(b)は許接断を示す図である。

代理人 舟理士 牧沢雄光

-545-

図1

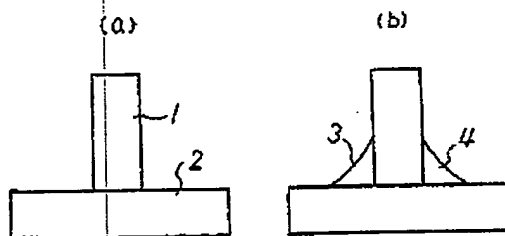


Table 1 - Filler Flux Components (Weight %)

Filler Flux Code	[illegible] Compound NaCl	[illegible] Compound																		
CF 1	0.1																			
CF 2	0.3																			
CF 3	1.8																			
CF 4																				
CF 5																				
CF 6																				
CF 7																				
CF 8																				
CF 9																				
CF 10																				
CF 11																				

1) Other components were K₂O₃, Ne _ O, Feo and [illegible] components.